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AND
KINDRED INDUSTRIES

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THE MANUFACTURE OF
VARNISHES
AND
KINDRED INDUSTRIES

BASED ON AND INCLUDING THE "DRYING OILS AND VARNISHES"
OF
ACH. LIVACHE

BY
JOHN GEDDES McINTOSH
LATE LECTURER ON VARNISH MANUFACTURE AT THE POLYTECHNIC, REGENT STREET, AND
THE BOROUGH POLYTECHNIC

VOLUME I.
THE CRUSHING, REFINING AND BOILING OF LINSEED OIL AND OTHER VARNISH OILS

THIRD EDITION, REVISED AND ENLARGED

WITH 114 ILLUSTRATIONS AND NUMEROUS TABLES

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REVISER'S PREFACE.

In presenting the enlarged and improved edition of Volume I. of "The Manufacture of Varnishes," it should be understood that the publishers found themselves in a position of some amount of difficulty through the sudden decease of the author, Mr. John Geddes McIntosh, just after the MS. was passed to the printers. Friends of the deceased author could testify as to his ambition for making what has ultimately proved to be indeed the crowning effort of his life. This would doubtless have been realised, bearing in mind the author's lengthy and unique technical and literary experience. Death—the great leveller of all men—has intervened, thus leaving to another the work of revision, which, he feels, even exercised with the best intentions, cannot rank with that of the pastmaster who has now let fall his pen. The reviser wishes it to be understood that every effort has been made to preserve throughout the style or form of expression characteristic of the author. That and the sequence of matter remains exactly as originally planned. It is, however, unfortunate that some gaps were found in the proofs, obviously intended for the insertion of additional and no doubt individual matter which experience only could dictate; and it may so happen that statements of inferences born of a life's experience are unintentionally omitted. The chief task of the reviser has been to give of his best towards discreetly closing up such gaps. If the presentment of the matter appears fragmentary, the indulgence of the reader must be encroached upon; remembering that books, like men, are not without virtues and vices. Allowing for the difficulties referred to, the reader cannot fail to be impressed with the fact that this work is without a rival, and as such will surely prove a useful book of study and reference to those engaged, or about to be engaged, in the technology of paints, varnishes, and allied materials.

CHARLES HARRISON, F.C.S.,
Registered Lecturer, etc.

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Borough Polytechnic Institute,
Borough Road,
London, S.E., *April*, 1919.

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HISTORICAL NOTE.

Early Use of Linseed Oil as a Vehicle in Oil Painting in England.—It is not to be suggested that linseed oil was first used as a paint vehicle and binder in England, but the usual statement that our knowledge of such use came to us through the Van Eycks is without foundation. In the Close Rolls is found an order issued by King Henry in the year 1239 ordering the payment of money for material and labour in painting the Queen's Chamber at Westminster, and from the mention of oil and varnish it may be safely inferred that the former, the oil, was used as a vehicle for pigments:—

"The King to His Treasurer and Chamberlain, Greeting! Deliver of our treasure to Otto the Goldsmith and Edward his son one hundred and seventeen shillings and ten pence for oil and colours bought and pictures made in the Chamber of our Queen at Westminster from the Octaves of the Holy Trinity in the twenty-third year of our reign to the Feast of St. Barnabas the Apostle in the same year, namely, for fifteen days." It has been suggested that these arrangements were made in view of the Queen's accouchement, as her first son, Edward, was born on the 16th of June, 1239, five days only after the first date mentioned in the record.

The following extracts are from rather later records. They give the materials used in the decoration of St. Stephen's Chapel and their prices from Rolls of the 25th of Edward the Third, that is, the year 1351:—

"July 18. To Master H. de St. Albans for four flagons of painters' oil for the painting of the chapel 16s. Sept. 5. For 19 flagons of painters' oil at 3s. 4d. per flagon £3 3s. 4d. (white and red lead, ochre, azure, vermilion, cole (size), white varnish, sinople and cynopre (the latter from Montpelier), gold leaf, tinfoil, squirrels' tails, hogs' hair, cotton for laying on gold). A pair of scales to weigh the different painters' colours is included.

CHAPTER I.

PROPERTIES OF DRYING OILS.

General Properties of Fixed Oils and Fats.—Although at first sight a fixed oil may appear to be a perfectly simple, homogeneous, elementary body, yet if we study any of these oils or fats attentively we will observe certain phenomena which indicate the complex nature of their constitution. If, for instance, we expose oil to a low temperature, it separates into a liquid and solid portion. Again, if we press tallow between folds of filter paper we express a liquid oil. But it remained for Chevreul to demonstrate by chemical means the exact constitution of these bodies. Chevreul submitted these oils and fats in a methodical manner to the action of different reagents, and found that they could be separated into different proximate bodies. He established the fact that every fixed oil or fat was made up of two or more fatty bodies of a greater or less degree of purity, each of these bodies differing from one another in their melting-points, fluidity, solubility in different menstrua, etc. He found, further, that each of these proximate bodies existing in oils and fats was really a salt, i.e. a compound arising from the combination of an acid with a base.

Chevreul pointed out that the different properties of oils and fats were due to the individual combined fatty acids, characteristic of each oil and fat, differing among themselves in composition and properties, but that the base was the same in all, or nearly all, cases, viz. glycerine. The fatty acids he found to be principally the following four, viz. stearic acid, palmitic acid, margaric acid, oleic acid; and that three equivalents of each of these monobasic acids combined with one equivalent of the triad glycerine to form respectively the salts, tristearine, tripalmitine, trimargarine, trioleine. The three former are solid at ordinary temperatures, the latter liquid. The tristearine forms the hard, solid portions of tallow and lard, and trioleine the soft oily portion.

He termed this resolution of the neutral fat into fatty acid and glycerine saponification. This decomposition for candle-making is brought about in various ways, the simplest of which consists in distilling the fat with steam superheated to 300° C., when the glycerine and fatty acids distil over together, the latter forming a layer floating on the former. The liquid oleic acid is then pressed from the mixed fatty acids, and a residue of mixed solid fatty acids obtained. The advantages gained by using a solid fatty acid instead of a neutral fat are many, including the raising of the melting-point by the elimination of the liquid oleic acid and glycerine. The bad-smelling, throat-irritating acrolein being a decomposition product of the latter, no smell is produced on burning. The candles do not smoke and no snuffing is required. But in the case of a drying oil the fatty acids do not dry so well as the original oil. Of late years the hydrolitic action of certain ferments or enzymes, e.g. lipase, has been used to split up oils and fats into fatty acid and glycerine. If the elimination of glycerine from a solid fat such as tallow results in obtaining improved products for candle-making, unfortunately it is not so with a drying oil like linseed oil, the fatty acids from which, owing to their being solid if not greasy, are not nearly so suitable for paint and varnish purposes as the original. But what are drying oils and wherein do they differ from non-drying oils?

Drying Oils. Definition.—The drying oils are those oils of vegetable origin which, being liquid at the ordinary temperature, possess the property of gradually and progressively absorbing oxygen from the air when exposed thereto in a thin layer whilst still at the ordinary temperature, and in so doing, instead of yielding a rancid, more or less viscous, greasy mass, naturally change gradually and eventually by insensible gradations from the original condition of a fluid oil into solid elastic dry substances insoluble in the usual oil solvents. The greater the quantity of oxygen which such an oil is capable of absorbing and fixing (when exposed to the air in so thin a film that the air can penetrate to the ultimate bottom layer of the film) as shown by the nett increase in weight, the greater are the drying properties and propensities of the oil. The greater the avidity with which a drying oil absorbs oxygen, and the greater the rapidity with which it solidifies and dries throughout its mass, *ceteris paribus*, the better is the oil. The more thoroughly, the more perfectly the thin film of pure linseed oil dries, the more intractable it is. Neither solvents, reagents, weather, nor even age affects it. The word nett is used advisedly, because linseed oil absorbs even far more oxygen than the amount it fixes permanently. This latter quantity of oxygen is used up in the formation of volatile compounds, carbonic acid (some say carbonic oxide), formic acid, acetic acid, oxalic acid, although the bulk of the oil, still existing as a glyceride, remains to form the dried film. The action of drying splits linseed oil up into two main divisions—one of these divisions liquid and volatile; the other fixed and solid. The volatile portion escapes into the air, the solid portion is fixed.

The sequel of changes which a drying oil undergoes during the time it is being converted (1) into an intangible volatile portion, which passes away into unknown regions, and (2) a tangible solid portion sensible to the eye and the touch, which remains fixed an manent, is termed the *drying* of the oil. As a matter of fact, the oil does not *dry* in the true acceptation of the term. When a substance in ordinary language is said to *dry*, what is meant is that the substance in question loses any adherent, adventitious or interstitial water or hygroscopic moisture, and, in a case of drying of that nature, we can appreciate the change, as it proceeds, both by the eye and the touch. The vapour is visible to the eye as it condenses, and the touch is sensible to the drier feeling as the moisture is expelled to a greater and greater extent. *Such substances, therefore, suffer a diminution in weight corresponding to the amount of water eliminated in the process.* But a phenomenon of quite an opposite nature occurs when a drying oil dries; instead of losing in weight it gradually becomes heavier as the "drying" process proceeds, until the oil has completely "dried," when its nett weight will be found to have increased some 16 to 17 per cent. In other words, 10 gallons of linseed oil, spread over any given surface, will not only increase the weight of the object on whose surface it was painted by the weight of the 10 gallons of oil, but, when the oil dries, the object will be found to have in all increased in nett weight to 110 lb., 93 lb. of which are due to the oil and some 17 lb. due to the absorption of oxygen gas from the air and its absorption by and permanent fixation in the oil. Now a gallon of oxygen weighs about 95 grains, and as there are 7000 grains in a lb., and as 17 lb. nett of oxygen were absorbed, we get a total of 119,000 grains of oxygen absorbed by the oil, which, divided by 95 grains, gives us nearly 1253 gallons of oxygen gas as being required to dry 10 gallons of oil. But the air only contains $\frac{1}{5}$ of its volume of oxygen, so that 6265 gallons of air are in this oxygen absorption phase totally deprived of oxygen by the drying of 10 gallons of linseed oil. This 1253 gallons of oxygen, be it well understood, actually enter into the constitution of the film of paint. Independent of the volatile decomposition products already named the absorption of oxygen by linseed oil is always accompanied by the evolution of a highly toxic gas known as acrolein which, when in a concentrated form, attacks the eyes and the nose as in oil boiling (weeping, running at the nose, etc.).

This diminution of the oxygen of the air and the evolution of acrolein are points in connection with the bad effect of sleeping in newly painted rooms which have not received from the medical faculty the attention they deserve. The headaches and other symptoms may, on investigation, prove not to be due to the toxic effects of turpentine and its oxidised derivatives, or to linseed oil emanations as a whole, but more to the rapid manner in which both linseed oil and turpentine diminish the proportion of oxygen in the superincumbent atmosphere by the energetic way in which they absorb oxygen. The fact that very possibly much of the glycerine contained in the glycerides of linseed oil is resolved into acrolein, points to the necessity of free ventilation from the open air. To cope with the evolution of acrolein the air should not be deprived of oxygen. To put a painter to paint in a room which has no direct communication with the open air is a dangerous proceeding. But there need be no serious effects provided ventilation be attended to, and this is best done by burning a fire in the room in which painting and varnishing operations are being conducted, and by discriminately opening the windows, avoiding at all risks and all hazards a damp cold draught playing on the surface being painted or varnished until some time after it has thoroughly dried. The doing away with fire-places and heating bed- and sitting-rooms by steam is much to be deprecated. *An ordinary substance in drying loses water and loses in weight. A drying oil in drying absorbs oxygen and increases in weight*, and that too in spite of the fact that linseed oil in drying generates acetic acid, carbonic oxide, carbonic acid, oxalic acid, and water. Moreover, if we can see the water being expelled from an object by the clouds of steam which are formed in the process, and although we may increase the rapidity of drying of linseed oil by the application of not too great a heat, such as "drying" the article in a hot-water oven, or a current of air, yet if our sense of smell tells us that vapour of some sort is being evolved, in no instance can this vapour be seen to rise from pure and good linseed oil, unless the heat be raised so as to start the destructive distillation of the oil. As just seen, aqueous and other vapours are given off by linseed oil in drying, but those vapours are due to the decomposition of the proximate constituents of linseed oil with the simultaneous absorption of oxygen, all of which finally result in the drying of the oil by the formation of the solid body into which linseed oil is resolved in drying, viz. linoxyn. If the oil contain spirits of turpentine, naphtha, etc., it will of course give off a considerable vapour of volatile solvent at a much lower temperature than unthinned linseed oil pure and simple.

When linseed oil in its pristine liquid condition is spread over the surface of an object which has been made impervious by the process known as priming, that is to say, its pores have been filled up in a suitable manner, it forms when dried an impervious coating, viz. the linoxyn just referred to, which still further protects the object from the effects of wear and tear and all those extraneous erosive agencies which we know under the term weather, such as the difference in temperature between day and night, summer and winter, heat and cold, rain, frost, and snow.

Linseed oil is unique in this respect; when dear, the carping critics whose pockets are touched have not got a good word to say in its favour and recite a whole decalogue of sins due to its use either *per se* or as an ingredient of paint or varnish.

The Function of Drying Oils as Vehicles for Pigments.—To increase the thickness of the coating, and also to form a harder, more permanent, more anti-corrosive and more anti-erosive layer, the drying oil is generally mixed with substances known as pigments. The oil, in drying, cements these pigments to the object to which the mixture of oil and pigment is applied. The mixture of oil and pigment is called a paint. The drying oil is said to act as the vehicle. We thus often hear of pigments and vehicles. But a vehicle would be of no use unless it acted as a lasting binding agent as well. Colza oil would form as good a vehicle for pigments as linseed oil, if not better; but as colza oil is a non-drying oil, the paint made by using it would not be a paint at all, as the vehicle would not dry, and thus it would not solidify itself, and hence it could not consolidate the particles of pigment and itself into a hard impervious layer, and the mixture would be more suitable for axle grease than for paint purposes. In the same way size, used in distemper painting, is a good enough vehicle for indoor work when applied to the walls of rooms, but the denuding and erosive action of the weather would render it worse than useless when applied out of doors.

The word vehicle as used by some writers is, therefore, an incomplete definition of the functions of a drying oil when applied in conjunction or in combination with a pigment to the surface of an object. It is the cementing or binding agent, or vehicle, if you will—just as slaked lime is the agent which binds the sand in the mortar to the wall. Not only so, just as the lime cements the particles of sand to themselves and to itself and the agglomerate thus formed to the wall, so also does the linseed oil cement the particles of pigment to each other and to itself and the agglomerate thus formed to the object to which it is applied. But the analogy does not rest here; the slaked lime also increases in weight in drying. Although it gives off moisture it nevertheless at the same time absorbs carbonic acid. For every 18 parts of chemically combined water which mortar gives off in drying and consolidating it absorbs 44 parts of carbonic acid, and consequently increases in weight, as we have just said.

Summary.—The function of a drying oil when used as a vehicle for paints is to so "dry" as to bind and consolidate the pigment in such a way that the combined layer formed by the dried vehicle and pigment, that is, by the dried paint, will withstand the heat of the sun's rays, the erosive action of the weather, and in conjunction with the pigment protect the object to which it is applied from the corrosive and erosive action of the same.

The Function of Drying Oils as Varnish Ingredients, i.e. as "Vehicles" for Resins.—The chief function of drying oils as ingredients of varnishes is first of all to dissolve the resin so as to bring it into the fluid condition; here again colza and other oils would act similarly, but the solution of resin in colza oil would never dry, and the only use for such a product would be for axle grease, and even for that purpose it would not be very fit, and not only so, it would be a very costly way of making axle grease. Here again the function of the linseed oil is to dry, and in so doing to cement together the particles of resin by an elastic binding agent consisting of the product into which the linseed oil is resolved on drying. The greater the quantity of linseed oil and the fewer the particles of resin which it has to cement together, and which are present in a "dried" coating of varnish, the more elastic and durable will be that coating. It is linseed oil which gives elasticity to varnishes. If a linseed oil substitute consisting of hydrocarbides, such as rosin oil, be substituted for a drying oil, e.g. linseed oil, whether in a paint or varnish, this durability and elasticity is lost, the dried product dissolves in weak solutions of alkali, and even in warm solutions of household soap, as is seen in the case of the front door of the housewife who must always be scrubbing. Her newly painted and varnished front door in a few months looks as if it had not been painted or varnished for as many years. Moreover, the melting-point of the dried product of linseed oil is high, as any one may satisfy himself by trying to melt linseed oil skins, but the melting-point of the "dried" (*sic*) product of hydrocarbide oils, e.g. rosin oil, is no better than that of common rosin. Moreover, the dried product of such oils or varnishes is soluble in the original varnish, especially in the sun, when the former melts, a fact which gives rise to many exasperating difficulties when it is desired to apply a second coating of the same paint or varnish on the same article. In the cool of the evening the coating may be as "dry as a bone," in the heat of the day it is simply a liquid pitch, and if the coating does eventually so dry and harden as to withstand the heat of the sun, it is such a mass of cracks and furrows that those on an elephant's hide might well be compared to them. These cracks and furrows are produced by the difference in temperature between day and night, producing hundreds of alternate liquefactions and solidifications of the coating, into the composition of which this linseed oil substitute enters so largely. Moreover, in the cool of the evening the coating seems to dry, but it is merely surface drying, underneath is a layer of liquid pitch like that of a lake of asphaltum, and it only requires the heat of the sun to melt the surface crust to liberate streams of the liquid confined beneath.

The great function and characteristic property of a drying oil is to yield on drying a coating of high melting-point, great elasticity, great imperviousness, and great durability when exposed to wind and weather, and resisting both natural and artificial reagents and solvents.

Dr. Ure, writing away back in the fifties of last century, differentiated between drying and non-drying oils. "Certain oils thicken and eventually dry into a transparent, yellowish, flexible substance; which forms a skin upon the surface of the oil, and retards its further alteration. Such oils are said to be *drying* or *siccative*, and are used on this account in the preparation of varnishes and painters' colours.

Other oils do not grow dry, though they turn thick, become less combustible, and assume an offensive smell. They are then called *rancid.* In this state, they exhibit an acid reaction, and irritate the fauces when swallowed, in consequence of the presence of a peculiar acid, which may be removed in a great measure by boiling the oil along with water and a little common magnesia for a quarter of an hour, or till it has lost the property of reddening litmus. While oils undergo the above changes, they absorb a quantity of oxygen equal to several times their volume." Dr. Ure might have said equal to half their weight.

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CHAPTER II.

THE PRODUCTION OF LINSEED OIL.

THE best-known and typical drying oil is linseed oil, a product of the seed of the flax plant *Linum usitatissimum*, a plant belonging to the natural order *Linaceæ*.

On examining the flower of the *Linaceæ*, e.g. the flax plant *Linum usitatissimum*, observe an inner whorl of five stamens imperfectly developed, indicated by short filaments without anthers. In some exotic allies the stamens are decandrous from the inner five becoming antheriferous. A cross section of the ovary exhibits, apparently, ten cells. There are really five, each of which becomes more or less "spuriously" divided by the infolding of the dorsal suture of each carpel. There is also a tendency to a *dimorphic* condition in some species of flax, manifest in the different relative lengths of stamens and pistil in different individuals of the same species; a natural contrivance to favour the crossing of the flowers by insect agency.

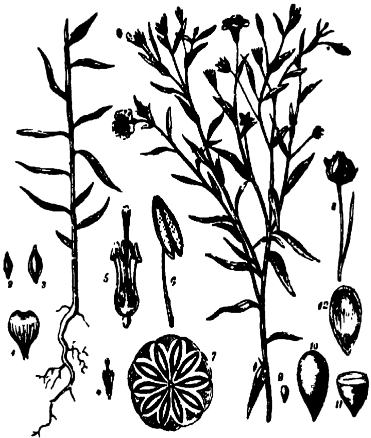


FIG. 1.—The flax plant (*Linum usitatissimum*), after Schädler. 1, flower leaf; 2, outer leaf; 3, inner leaf; 4, 5, organs of fructification and pollen vessel; 7, cross section of capsule; 9, 10, 11, 12, seed, natural size and enlarged; cross and longitudinal sections.

The flax plant *Linum usitatissimum* is a native of Europe and Africa, and indigenous to Britain. The term *usitatissimum* is well merited. The flax plant has been cultivated from very ancient times, having been grown by the Israelites so far back as when they were in Egypt. Flax is cultivated for two objects, firstly, for its stem, which yields by maceration the tenacious fibres used in the manufacture of linen, now of such vital importance in the manufacture of aeroplanes that attempts are being made to resuscitate flax cultivation in Great Britain; this should never have been allowed to die out. Secondly, for its seeds, which by expression, or extraction by means of solvents, yield (*a*) linseed oil and (*b*) the cake or meal obtainable as a residual from oil crushing or extraction, a valuable cattle food, which when passed through the stomach of an animal becomes a rich and valuable manure. That is to say, as a fertiliser the manurial excreta is almost as valuable as the oil cake itself was as a cattle food. Besides, the seed contains a valuable demulcent and emollient mucilage, which is of great importance medicinally, and, when made by the action of boiling water into a mucilaginous drink for calves, is an excellent substitute for their mother's milk.

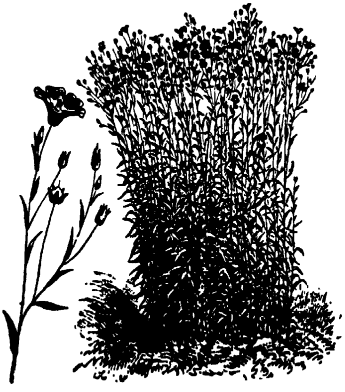


FIG. 2.—Spray of flax. Collective mode of growth.

The Cultivation of Flax in Great Britain.—Flax loves a deep, friable, rather moist soil. It grows well upon land newly broken up from pasture. In Ireland it is usually sown by the small farmers after potatoes. A fine, nicely pulverised seed-bed is essential, and this is rolled after the seed is sown. The usual time of sowing is from the middle of March to the end of April. Dutch seed is in the highest estimation, affording a greater produce than the American seed, and a finer quality than the Riga. The after-cultivation consists in taking up the weeds by the hand—the only way in which it can be done, and a tedious process if the land be at all foul. The crop is raised by pulling up the plant by the roots. The fruit is a capsule with 10 seeds, 3½ to 5½ millimetres long. The produce in seed is from 6 to 8, and sometimes as high as 10 or 12, bushels per acre. The best of it is kept for sowing again, and the next quality is crushed for oil. Flax, when allowed to ripen its seeds, is a very exhaustive crop, even more so than corn, and in most parts of Britain is so little understood that its cultivation has of late been very limited. But a great deal of flax was at one time raised in Ireland. Its cultural zone is almost world-wide. An extension of the area under cultivation at home, in India, and other dominions beyond the seas is urgent.

If superior fibre be desired, then the flax must be harvested before the seeds are ripe, and the seeds are then small in size and poor in oil. Although linen fabrics are superior to cotton the utilisation of flax fibres is in most countries quite a secondary matter to that of the seed. The world's production of linseed amounts to about 3 million tons yearly. The chief producing countries are India, the U.S.A., Argentina, La Plata, Russian Baltic, Black Sea. Smaller quantities are furnished by Egypt, Roumania, North of France, Denmark, Holland, Belgium, and Hungary.

Linseed Oil Mill Cross-Section.—This section shows roughly the methods adopted in the most modern and up-to-date mills for landing and warehousing oil seeds from ship or barge, lying alongside the oil mill wharf. In the first place, the ship elevator is movable on a longitudinal tramway, so that the elevator can be moved about from point to point, and the barge completely discharged even when it is aground. In connection with the tramway, there is a longitudinal band for taking the seed into the elevator in the cleaning and weighing house. The cleaning and weighing house would be arranged in accordance with the demands of the trade, but generally would be as follows: The elevator would lift the seed into a hopper over the weighing machine; from the weighing machine it would fall into another hopper, and from thence would pass to the cleaning machinery; from the cleaning machinery it would pass to the main elevator in the silo house: from the main elevator it would be delivered to band conveyors, which would take it to any of the bins in the silo house. These bins would be arranged to discharge again to band conveyors, which would again deliver to elevators, and so to the bins over the Anglo-American rolls in the mill. The bins in the mill would be so arranged that they would hold enough seed for the night shift, when all the silo house and other machinery could be stopped.

Machinery for Cleansing Linseed. The Magnetic Separator, its Use and Action. 1. *Use.*—The magnetic separator is largely used in oil seed crushing mills for separating magnetically any stray pieces of iron or steel, e.g. bolts, nuts, nails, hammer heads, and such like from seeds or nuts previous to being ground and reduced, thus obviating stoppages and complete breakdowns.

2. *Action.*—The seeds or nuts are fed on to a shaking tray

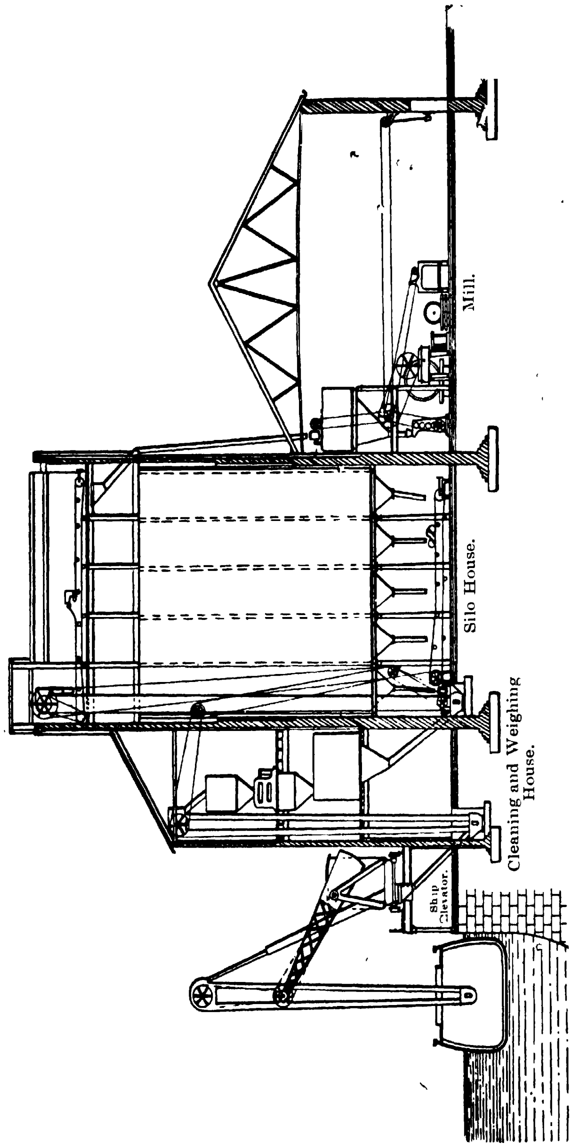


FIG. 3.—Cross-section showing landing machinery, cleaning machinery, silo house and mill.

(covered with sheet steel) which distributes the feed evenly and forces the iron or steel to sink by gravity to the bottom of the stream, which then passes over the revolving magnetised cylinder, the non-magnetic material falling down in front whilst the stray pieces of iron or steel are carried round past the bottom and released and dropped at the back.

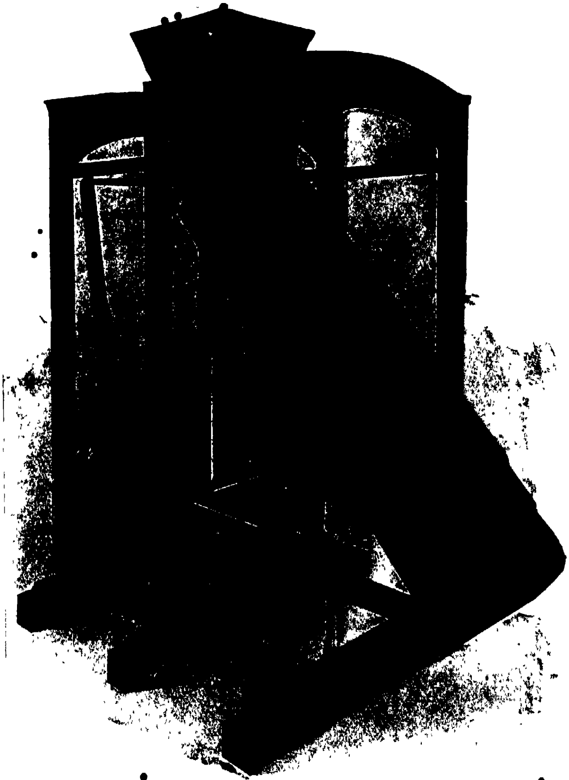


FIG. 4.—Magnetic separator for separating fragments of iron from linseed.

The release is effected in a very simple manner by two commutators (one at each end) breaking the electric current which circulates round the magnet coils at the moment each row passes the bottom. These commutators also connect each row as it comes to the top, thus magnetising them again.

Machinery for Screening Linseed.—Sometimes the screens are circular. Such screens are used to free linseed from dust and lumps. The barrel or body of the screen revolves in an inclined position, the higher portion of it being covered with wire gauze sufficient to retain the seed but to allow the dust to pass through. The lower part of the screen is made of wire of such a mesh as to let the linseed pass through, while retaining any lumps or pieces of metal. The latter pass out at the end of the barrel. Such a screen will cleanse 3 to 28 cwt. of linseed per hour according to capacity.

Crushing Rolls.—The seed passes from the cleaning machinery to the rolls or crushing mills where it is ground into meal. The meal is then elevated into the kettle or heater where it is heated and tempered, this operation facilitating the flow of oil when in the press, whilst much albuminous matter is solidified.

Moulding Machine.—From the kettle the heated and tempered meal is drawn off into the moulding machine or former, where it receives a preliminary pressing before being pressed in the Anglo-American presses. As the cakes are moulded or formed by the moulder they are taken from this forming machine on steel trays provided for the purpose.

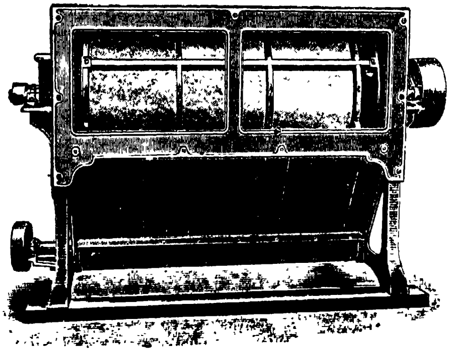


FIG. 5.—Screen for freeing linseed from dust, dirt, sand, grit, and metals. The use and action of this machine are so obvious as to render description superfluous.

Presses.—As soon as one press has been filled by the pressman in this manner he turns on the hydraulic pressure to the press from the pumps or accumulators, as the case may be. As the pressure rises in the press the oil begins to flow from the compressed meal, at first slowly and then very rapidly, gradually ceasing when the bulk of the oil has been removed; and when the pressure has been on 3 or 4 minutes the flow of oil practically ceases, the oil simply dripping away from the now compressed cakes until the pressure is turned off. If more presses than one are being used they are filled one after the other until the whole battery of presses is charged. The presses are allowed to remain under pressure for a fixed period, which varies under special conditions from 10 to 40 minutes, and when the proper time has elapsed the first press is turned down, i.e. the pressure is turned off and the ram allowed to descend, the cakes being removed one by one as the ram descends and fresh charges of meal introduced wherever a cake is removed. As the cakes are removed they are placed on a table near the paring machine. The man operating this paring machine then strips off the bags from the cakes, and pares the oily edges away from the cakes by means of the paring machine, these oily parings being reduced to meal again and returned to the kettle to be again worked up. The pared cakes are placed in racks in which they are allowed to stand until perfectly cool, when they can be removed to the cake house or store, to be stocked or delivered to customers as occasion demands. The cake racks are usually allowed to stand in the most draughty part of the mill to assist the cooling process. In a like manner other similar small seeds would be treated, as, for instance, sunflower, mustard, china beans, some kinds of rape, poppy, and such other seeds as require a single pressing only.

THE CRUSHING OF LINSEED.

Rolls.—The first process in crushing linseed is to pass it through the rolls. It is conveyed to the hopper by an elevator or chute and distributed to the rolls by a fluted feed roll the same length as the feed rolls at the bottom of the hopper. From the feed roll it falls on a guide-plate, which carries it between the *first* and *second* rolls. After passing between these rolls and being partially crushed it falls on a guide-plate on the other side, which carries it between the *second*

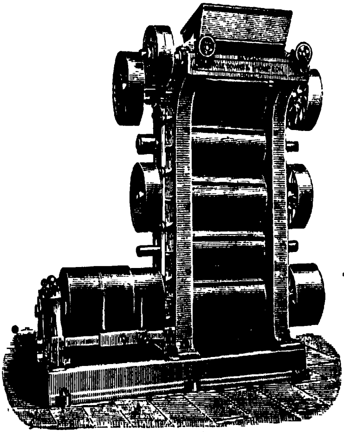


Fig. 6.—Rolls for crushing linseed.

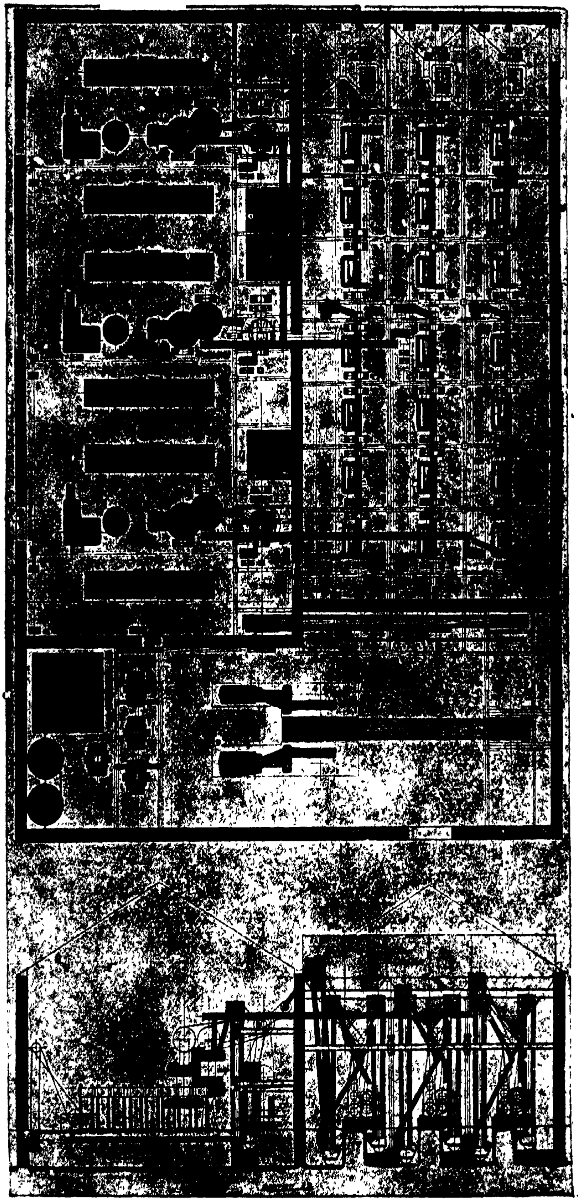


FIG. 7.—Oil mill, with 48 Anglo-American presses.

and *third* rolls, where it is crushed more fully. It then falls on another guide-plate, which carries it between the *third* and *fourth* rolls, where it is ground more fully still. In the larger rolls it falls on a fourth guide-plate, where it is conveyed between the *fourth* and *fifth* rolls and receives the final grinding. The seed is thus crushed four times in its passage through the rolls, which, being brought into contact by a combination of a screw and spring, give a smooth and easily regulated pressure. When the seed falls from the bottom roll the grinding is found to be much more complete and perfect than in seed that has passed through rolls and under stones of the old description.

The crushing of linseed resolves the seed into two components: (1) oil, (2) cake. Linseed only requires to be pressed once. The reason for this is because the cake is the most valuable feeding stuff which a farmer can use, and its best preparation for use as a manure is to pass the cake through the stomachs of cattle. By so doing the value of the cake as a fertiliser is reduced very little. The seed is therefore resolved by crushing into linseed oil and linseed oil cake; the cake after passing through the stomachs of cattle excels as a fertiliser. In order to secure the best results in the crushing of linseed, thereby obtaining pure oil and a cake that will pass the scrutiny of the agricultural chemists, one or two matters must receive proper attention at the outset. (1) The seed must be perfectly clean and free from earth, sand, grit, and other extraneous matter. (2) The seed must be free from all other seeds than linseed. (3) Oleiferous seeds of the type of non-drying oils reduce all those chemical and physical constants which are typical of linseed and drying oils, besides being objectionable by impeding drying. Linseed is sold generally on a basis of 95 per cent. purity and even as high as 97 per cent. When crushing linseed of this degree of purity it is not deemed necessary to attempt to clean it to a greater extent. But lower grade impure linseed is screened by passing through sifting machinery. (4) Linseed oil may be contaminated with non-oleiferous seeds, or seeds that are approximately so, which must lower the yield of oil obtained on crushing *pro rata*.

Steam-heating Kettle and Moulding Machine.—The meal heating kettle is made from steel boiler plates—not from cast iron—is 5 feet 6 inches diameter by 3 feet 2 inches deep, and it is steam-jacketed round the sides and bottom. The stirrer is actuated by self-contained driving gear—belt driving pulley, bevel wheel, pinion, vertical and horizontal shafts of polished steel, the whole being supported by a strong bracket fitted with gun-metal bearings fitted to the top of the kettle. The kettle is fitted with: (1) internal steam spray for moistening the meal with control valve; (2) steam pressure gauge; (3) control valves for steam and condensed water; (4) automatic shutter. The kettle is covered with hair-felt, for retaining the heat. Coating, for the sake of neatness, is covered by sheet iron. The kettle itself is supported by a pair of strong cast-iron brackets, which are securely bolted to the mill-floor, thus preventing all vibration. As the kettle is made from boiler plates, instead of cast iron, a much greater steam pressure can be sustained, without danger, so the crushed seed can be treated at a higher temperature, if need be. The system of cast-iron kettles has been discarded for some time as being liable to fracture, explosion, and leakages. Superimposed two-decker kettles are made to meet special requirements.

Fig. 8 is a vertical section of the steam kettle of Hallette, and *a* is the wall of masonry, upon which, and the iron pillar, *b*, the pan is supported. It is enclosed in a jacket, for admitting steam into the intermediate space *d*, *d*, *d*, at its sides and bottom; *c* is the middle of the pan in which the shaft of the stirrer is planted upright, resting by its lower end in the step *e*; *f* is an opening by which the contents of the pan may be emptied; *g* is an orifice into which the mouth of the hair or worsted bag is inserted, in order to receive the heated seed, when it is turned out by the rotation of the stirrer and the withdrawal of the plug *f* from the discharge aperture; *h* is the steam induction pipe; and *i* the eduction pipe which serves also to run off the condensed water.

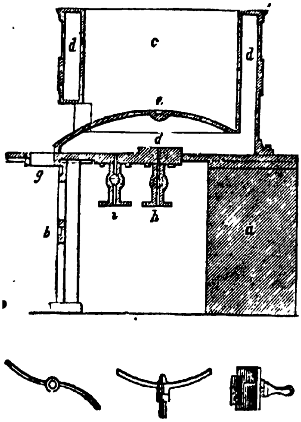


Fig. 8.—Hallette's steam kettle.

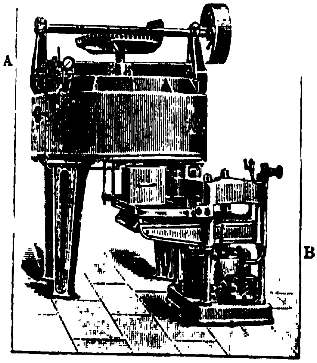


Fig. 9.—A, steam kettle; B, moulding machine.

After passing through the rolls the seed falls into a screw conveyer, which places it in an elevator that raises it to the steam-jacketed kettle (Figs. 9, 10), where the seed is heated and damped by a jet of steam and agitated by a revolving stirrer. These kettles are of cast iron, and are constructed in the strongest and best manner. There is only one steam joint in them, and that is faced in a lathe or planed quite true. There is, therefore, little liability to leakage—always a dreadful nuisance. When lagged, the kettle body is fitted with a wooden frame, covered with felt, and the felt is enclosed in iron sheathing. Up to this point the operations are automatic.

Hydraulic Cake-forming and Moulding Machines.—Like the kettle these machines are quite self-contained. They are used to measure the exact quantity of heated meal from the kettle sufficient to form one cake. This quantity of meal is subjected to a preliminary pressure previous to being placed in the hydraulic press. The machine is fitted with a balancing measure frame, made of hardwood lined with sheet steel, and is complete with meal strickling box, etc. The compression is imparted by a hydraulic cylinder fitted with a ram

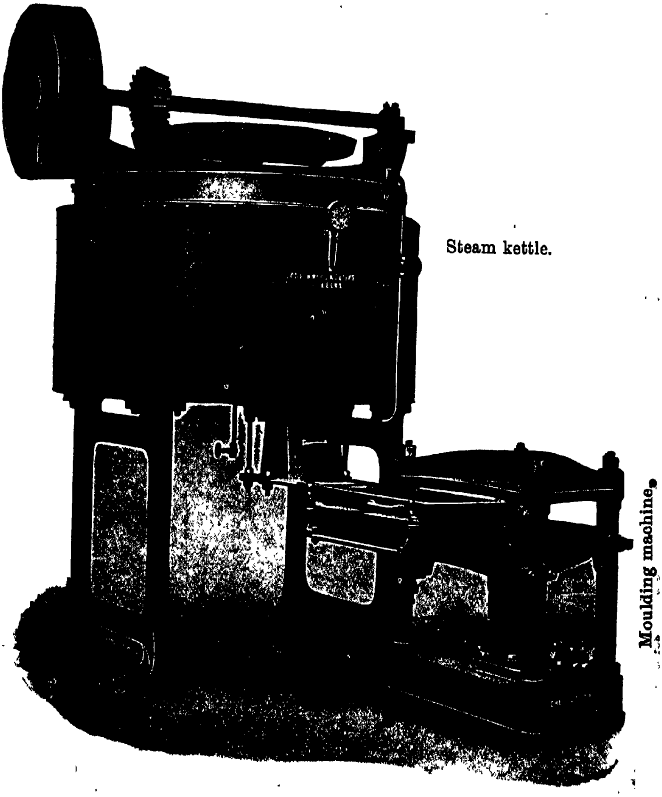


FIG. 10.—Seed heating kettle and cake moulding machine.

6 inches diameter, working in connection with the low pressure accumulator at a pressure of 500 to 700 lb. per sq. inch, such pressure being generally sufficient to show a film of oil on the press cloth, the seed prior to compression being about 3¼ inches deep, and being reduced by pressure to about 1¼ inches. Each machine is fitted with improved automatic arrangement for giving the pressure. With this type of moulding machine one man can with perfect ease measure, mould, and compress sufficient cakes for four presses, making 64 cakes in 20 minutes.

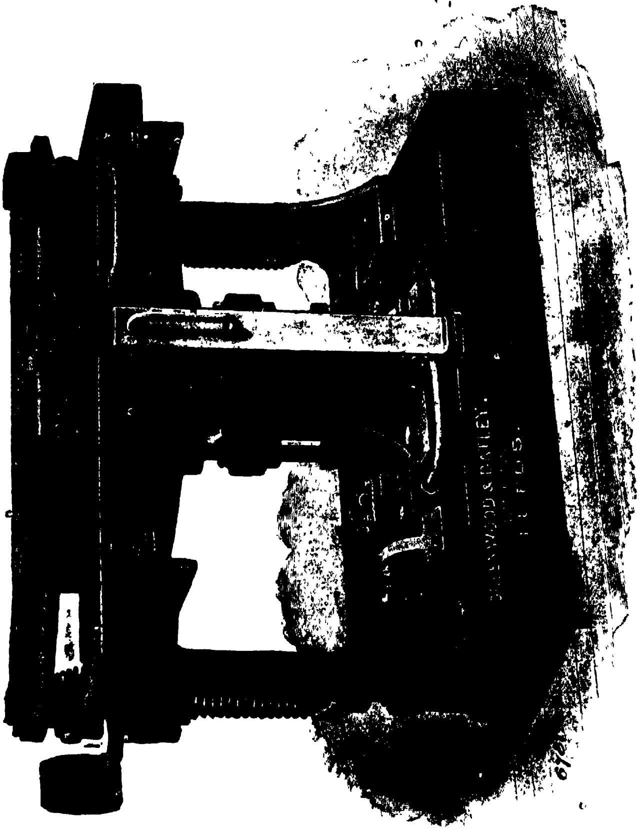


FIG. 11.—Hydraulic cake-moulding machine.

The automatic moulding machine is worked direct from the low-pressure accumulator, and possesses the following important advantages over the ordinary type of machine:—

1. *Greater Capacity and Output.*—Working in conjunction with

a four-decker kettle it is capable of heating and moulding sufficient cakes for sixteen Anglo-American presses, making 256 cakes every 35 minutes. A double kettle and automatic moulding machine is equal to two kettles and two moulding machines of the old type.

2. *Labour Saving.*—There is a great saving. Only one man is required to mould the cakes for sixteen presses as against four men with the ordinary type of machine.

3. *Efficiency.*—The work is better and more satisfactorily done than by hand moulding, and the cakes, besides being pressed from top and bottom, are also compressed at sides and ends, so that the seed is not apt to spread when pressed in the hydraulic press.

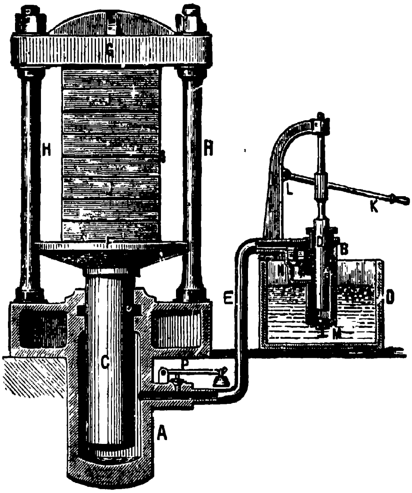


FIG. 12.—Showing the internal working of a hand-wrought hydraulic pump and press.

4. *Economy of Mill-floor Space.*—This is considerable.

5. *Cost Liquidated by Saving in Wages.*—If the first cost of the double kettle and automatic moulding machine is slightly greater than the cost of two ordinary kettles, yet the saving in wages, say 50 to 60 shillings per week, working day and night, pays an enormous interest on the increased cost.

The automatic moulding machine is now, on account of its many advantages, gradually replacing the ordinary hydraulic or steam-moulding machine. In the largest oil mill in this country there were until recently twelve automatic moulders, each with three kettles, serving ninety-six standard Anglo-American presses, when six more of these machines, each with four kettles, were installed, both kettles and moulding machines working in conjunction with another set of ninety-six presses, each moulding machine feeding a battery of the presses. It is advisable to install two, three, or four-decker kettles, according to the number of the presses to be served, so as to ensure better heating and moistening of the meal than when a single kettle is used. The result of this method of working is that the yield of oil will be considerably increased, the amount of oil left in the cakes being of course correspondingly less with a larger percentage of moisture.

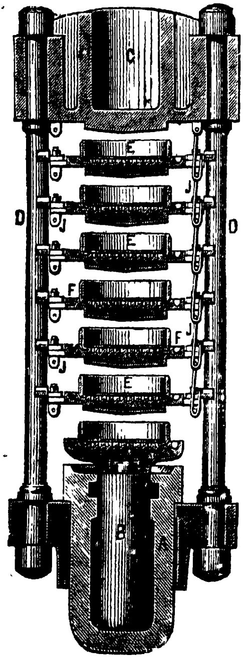


Fig. 13.—Sectional drawing of a German oil press.

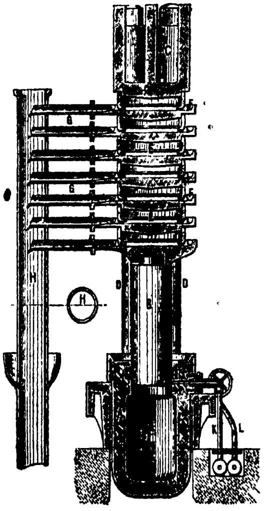


Fig. 14.—Showing a longitudinal sectional view of the circular cake oil press shown in Fig. 13 after the press boxes have been charged and pressure applied. Note the new position of the ram B and the collection of the oil in F from which it flows by spouts G to H.

The bags containing the seed are placed in the cavities of the shelves or press boxes EEE and then the ram B starts working. As it ascends, each bag is energetically compressed between the base of the press box containing it and the projecting bottom of the box next above it. To resist the pressure the head piece C of the press is supported by stout pillars. The oil runs out into the circular grooves FF and thence to delivery spouts JJ, and thus through the pipes to the vertical oil shoot H leading to the oil reservoir.

The hydraulic press as used in oil crushing and how it acts will be readily understood from a careful study of Figs. 12, 13, and 14.

The press installation below shows two sets of the latest and improved type of "Premier" presses as used in one of the most important oil mills in England. Each set consists of two presses having "cages" or cake chambers 19 inches diameter and 9 feet long internally. Each press has its own kettle 5 feet diameter by 2 feet 2 inches inside dimensions; the whole installation is constructed, in fact, on the most modern lines and is suitable for a working pressure of 3 tons on the sq. inch of the ram. The presses illustrated are for the moment engaged on the first pressing of castor seed. The seed is fed whole to the kettles heated by steam to a temperature of about 90° F. and afterwards pressed in the presses to the pressure indicated. The resulting cakes contain only 10 per cent. of oil and frequently less, recent analyses showing only 8·5 per cent. of oil remaining in the cake. The percentage is on the weight of the cake, and not on the total amount of oil in the seed prior to crushing.

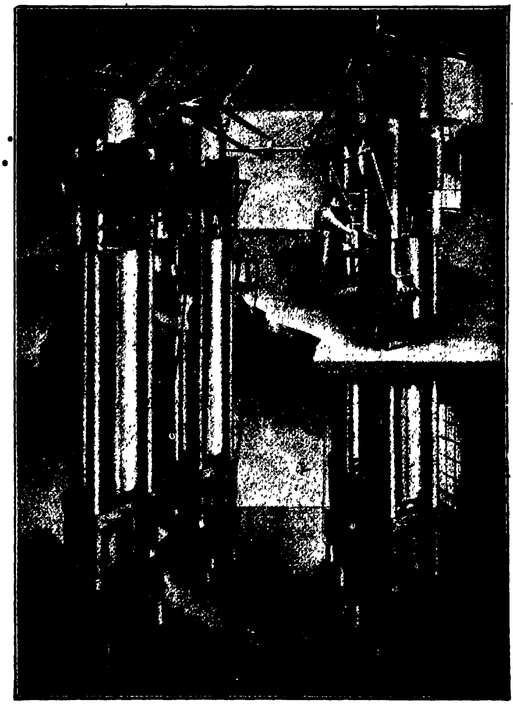


FIG. 15.—"Premier" presses.

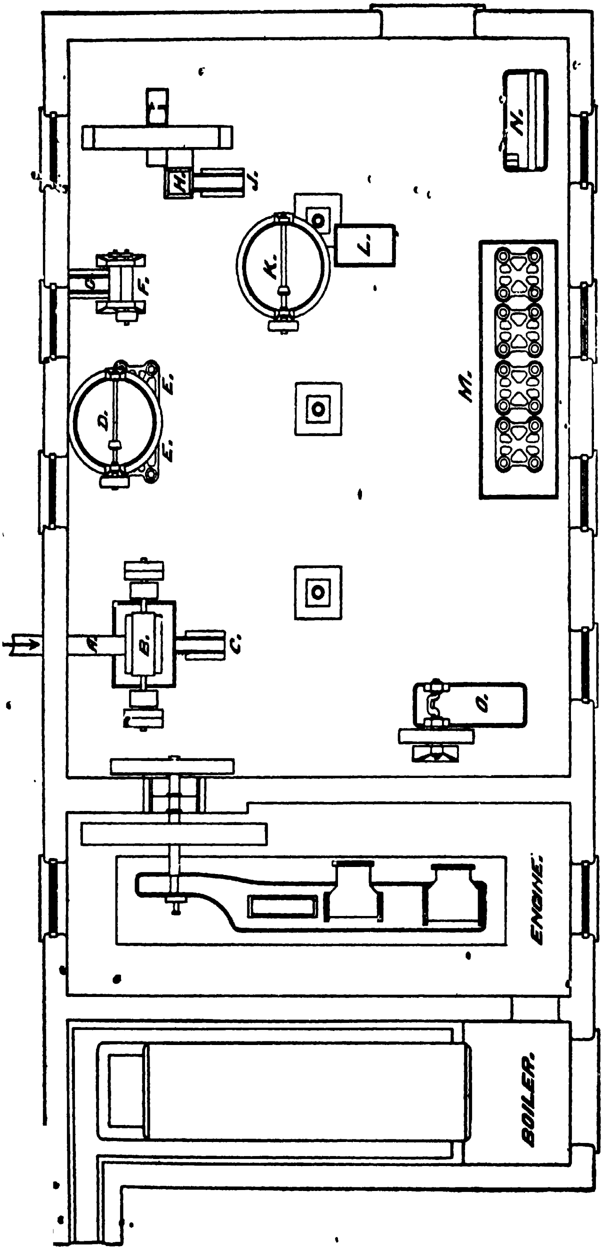


Fig. 16.—Ground plan "Anglo-Premier" mill for oil seeds requiring twice pressing.

These mills are on the Anglo-American system worked in combination with "Premier" presses, and are designed for expressing the oil from seeds and nuts which require two pressings, the first of which may be either hot or cold.

The mill illustrated in the plan is designed for the working of ground nuts, sesame (gingelly), and other similar small oil seeds, and consists of a No. 4 Anglo-American mill working in combination with a pair of "Premier" presses.

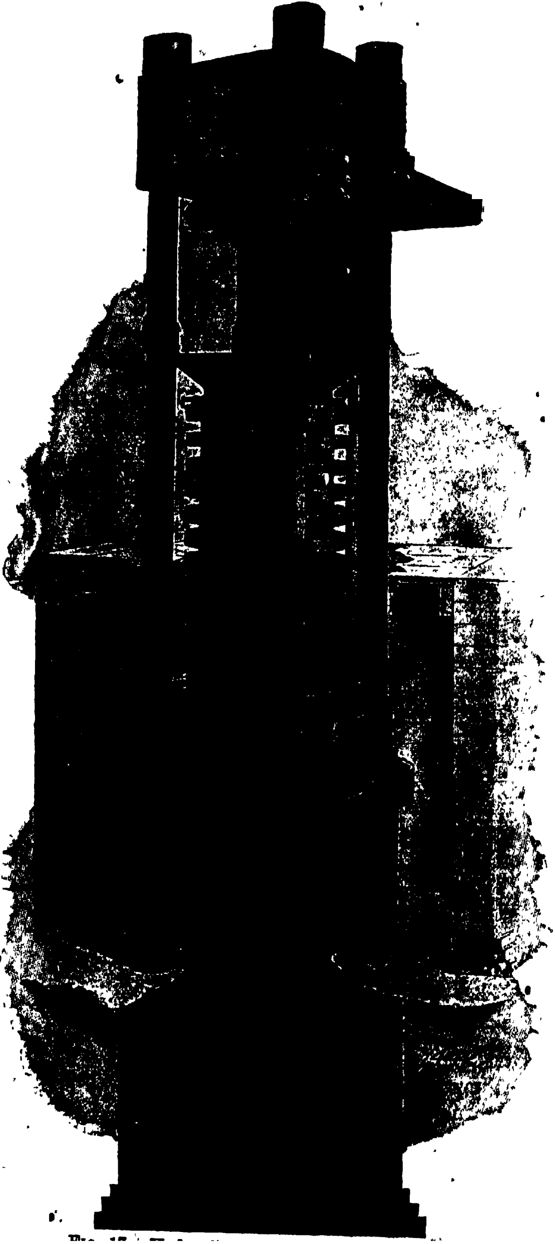
The process is as follows: The seed to be treated enters the mill at point A, and is ground by a set of Anglo-American rolls B; the rolled seed is placed by the elevator C into the kettle D of the "Premier" presses and the first pressing effected in these presses EE. The cakes from this pressing are then broken up by the cake-breaker F, and falling into the elevator G, are fed into a disintegrator H, which reduces the broken pieces to meal, which is placed by the elevator J into the Anglo-American kettle K, from which it passes through the moulding machine L to the Anglo-American presses M (four in number). The paring machine is shown at N, and the pressure pumps at O.

These mills are made up to any size, the above being a single block or "unit". They can at any time be worked on the ordinary Anglo-American system for linseed, cotton seed, etc.

The hydraulic presses on the "Leeds" system are specially designed for pressing the oil from palm kernels, copra, castor, sesame, ground nuts, East Indian rape, German rape, poppy seed, etc., and are equally suitable for cold or hot pressing. Owing to the high percentage of oil contained in the above seeds and nuts, it is only possible to extract the oil efficiently when the meal is confined during the time it is subjected to pressure in a pressing cage on the "Leeds" system. Hydraulic presses on the Anglo-American and similar systems are unsuitable for any kinds of seeds or nuts which yield more than 35 per cent. of oil in the first pressing, owing to the difficulty of keeping the meal from spreading and escaping to a large extent from such presses immediately it is subjected to pressure. Hydraulic presses on the "Leeds" system are usually worked in batteries of two, three, or four presses receiving their supply of meal from one kettle, the latter being suitable for working the meal either in a hot or cold state. The presses possess the following advantages:—

1. The pressing is practically continuous with the exception of the time required for emptying and filling the pressing cages, the remaining presses being in the meantime under pressure.

2. The improved "Leeds" pressing cages are so constructed that the meal when under pressure is retained in the cage, the oil in the meantime being extracted and flowing freely through the minute slits of the cage, falling by gravitation into the receptacle at the bottom of the presses and thence into a special settling tank. The edges of the pressed cake do not require paring. The quantity of seeds which may



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escape from the cage during the process of pressing is reduced to the minimum. An enormous saving of press cloths or mats (approximately 50 per cent.) in comparison with those used in Anglo-American or similar presses. Easy manipulation and economy in labour, no skilled men being required. For working four of the largest sized presses only three or four men are required.

Each press holds sixteen cakes, and is furnished with steel cylinders 16 inches in diameter, which carry a working pressure of 1¾ tons on each square inch of the ram. All the columns, cylinders, rams, and heads are planed and turned accurately to gauges, to ensure that every part will take its due proportion of strain and no more; the pockets that take the columns are not cast as is usual with fitting strips top and bottom, but are all solid throughout, and are all machined out of the solid to gauges.

Pumps.—The pumps for working the presses in the Anglo-American system of oil crushing are made of the highest class of crucible cast steel, and are all bored out of the solid. Two of the pump rams are 2½ inches in diameter and have a stroke of 7 inches. These rams give only a limited pressure, and the arrangements are such as to give the limited pressure on each press in about 14 seconds. The pumps then stop automatically. The work is then taken up by two other pumps having rams 1 inch in diameter and a stroke of 7 inches, and is continued by them until a gross pressure of 2 tons per square inch is attained. This is the maximum and is arrived at in less than a minute. The oil as it comes from the presses falls into the tank underneath, which serves as a foundation for the presses, and is pumped from there into the store cisterns.

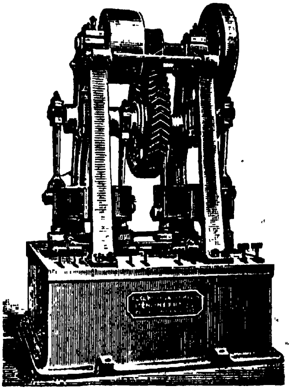


FIG. 18.—Hydraulic pressure pumps.

The cake plates between which the meal is pressed are all well fitted and have a corrugated surface. If a brand be required on the cake, say, letters about 3 inches long are clearly cut into one side of the plate and all the remainder is corrugated. These plates are all made of wrought and cast malleable iron.

Cake Paring and Moulding Machine.—The cakes require paring. The parer strips his cake and lays a number of these on a stool or table. He takes up one and lays it on the machine, having one side parallel to the trough and overlapping it about an inch, one end being placed against a fence, either to the right or left, depending on what stroke the machine is taking. The knife block passes along and cuts one side clean and straight. The cake is now turned over and the other edge treated in a similar manner. He now turns the cake half

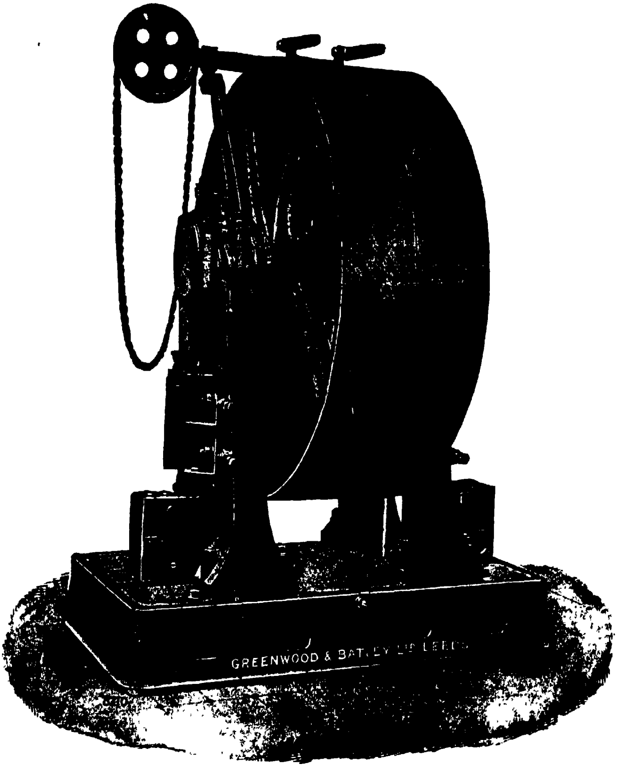


FIG. 19.—Hydraulic pump.

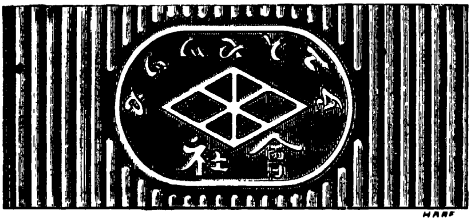


FIG. 20.—A rectangular cake plate with Japanese brand.

round, places one side against a fence, and cuts off the oily part at one end then reverses the cake and does the same with the other end.

The cake is now ready for the market, and has been pared by two double strokes of the knives, the speed of which is about thirty per minute. Fences or gauges may be added to give all the cakes one exact length and breadth, but these make more parings, as the fences have to be set to suit the worst cakes. These machines can be driven by a shaft either parallel with or at right angles to the knife bar, and are suitable for paring either parallel or taper cakes.

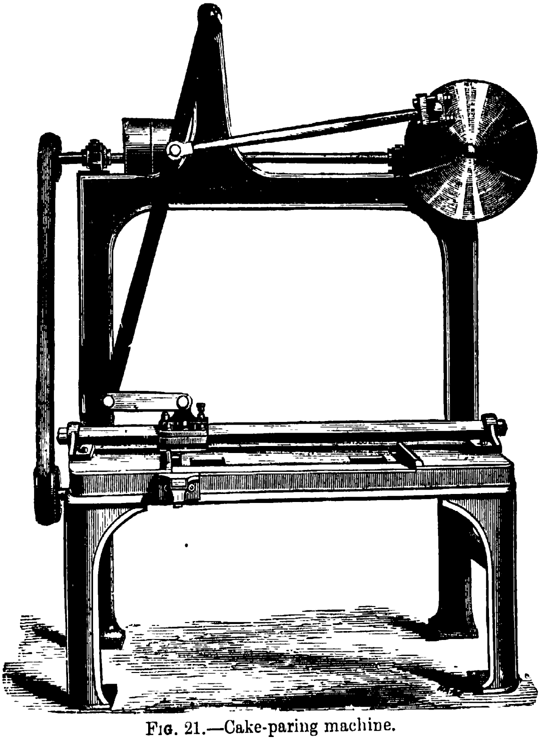


FIG. 21.—Cake-paring machine.

The Double Paring Machine.—This machine is designed to pare the pressed cakes from the presses to one uniform size and suits either taper or parallel cakes. All the moving parts, with the exception of the driving pulleys, are under the table, this system securing great steadiness in running. The parings, after they are cut from the cakes, drop into a central trough (in the table) fitted with a worm conveyer which carries the parings automatically to the paring stones and with improved chopping knives which break up the parings. Each paring machine is suitable for paring the cakes from two sets of Anglo-American presses, producing 256 cakes per hour, two attendants being required, who also strip the press cloths from the pressed cakes.

The single paring machine is identical with the above except that it is suitable only for paring the cakes from one set of Anglo-American presses, producing 128 cakes per hour, one attendant being required.

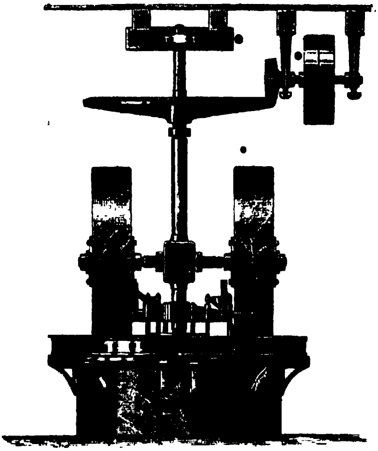


FIG. 22.—Edge runner. Front view.

Combined Paring and Triturating Machine.—This machine is dentical with previous ones, but is fitted with improved machine for triturating or granulating the cakes from four Anglo-American presses, producing 128 cakes per hour.

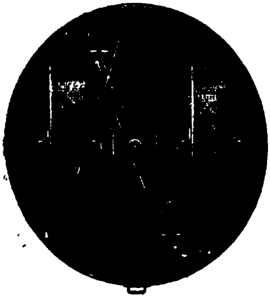


FIG. 23.—Edge runner. Plan.

Edge Runners for Grinding Cake Parings.—1. Gear driven from above (Figs. 22 and 24).—The parings are taken to the edge runners to be ground. These are made of the best Derbyshire grit stone, and are furnished with a set of cast-iron centres. One centre has a long boss on it, which passes right through the stone and the centre on the opposite side, and has a long brass fixed on each end of it. These entres are securely fixed to the stones with bolts that pass through hem, and they are also run into the stones with lead or cement. On the outside centre there is a cap fixed with screws, quite oil-tight, and large enough to hold several pints of oil. The spindle on which the stone revolves passes through the centre of the upright shaft, and the stone centre has a cap fixed on each end of it with cotters. These caps are enclosed in the oil-cups described above, and revolve among the oil contained in them, thus causing such a perfect lubrication of the spindle as to make it quite unnecessary to withdraw it oftener than once in several months. The casting that carries the vertical shaft passes through the bed-stone and goes beneath it, projecting beyond its circumference at six points, where it is attached to the circular pan above by six brackets. The top of this casting is fitted with a "step," constructed in several parts, which can be removed or replaced in a few minutes without disturbing the driving wheels. The vertical shaft is made of cast iron, about 7½ inches in diameter, having an oblong chamber or navel formed in the centre, into which is fitted a strong cast bush having a brass bush at each end through which the stone spindle passes. The bush is free to rise and fall in the navel as material is added to or taken from the stones. All the sweepers and sweeper frames are made of wrought iron. The circular pan is made of cast iron, dished slightly, and having a rim round its circumference 7 inches deep. All the bearings are brass, made very heavy and

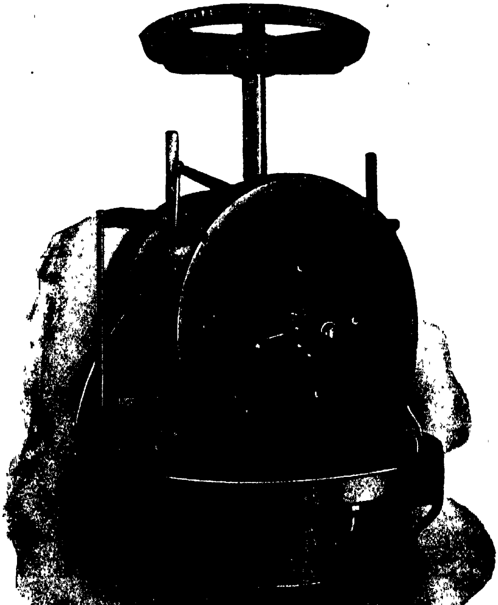


FIG. 24.—Edge-stones.

unusually long. The ground parings are carried from the edge runners by a conveyer, from which they fall into the seed kettle.

2. Belt driven from underneath (Fig. 23).—These stones are constructed in a similar manner to ordinary edge-stones, but are provided with two carfe plates instead of one. The higher carfe plate is perforated so that the material that is being ground may pass through it as soon as it is sufficiently pulverised, when it falls on the lower plate, where it is gathered together and discharged through a shuttle at any convenient point. The fineness or coarseness of the perforations regulates the texture of the ground material. For grinding anything that has to be reduced to an almost impalpable powder, these stones are unsuitable, but for grinding any material that is improved by being kept slightly granular they are invaluable, as they do much more work than ordinary stones, and can be arranged to feed and deliver in a self-acting manner. They are used principally for grinding cake parings, which they reduce to meal ready to be returned to the kettle.

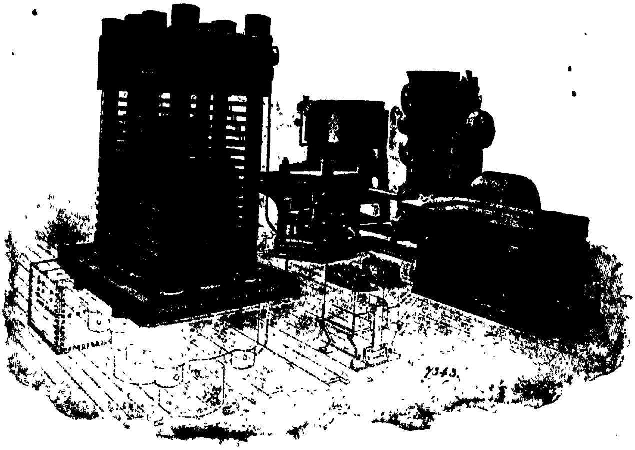


FIG. 25.—Self-contained Anglo-American oil mill, to crush and press about 50 tons of linseed, cotton seed, ravison rape, soya beans, sunflower, mustard, niger, and similar seeds, per week of 132 hours.

The Bathurst Kettle Controller.—This appliance is to prevent the erratic charging of presses whereby the quantity of meal in the kettle is constantly varying, with the accompanying result that the temperature and proportion of moisture also varies so as to seriously affect both the yield of oil and the appearance of the cakes. It has been specially designed for use in conjunction with the patent automatic kettle and cake-moulding machine, each of which easily forms the cakes for eight ordinary 16-cake presses and requires only one attendant, but it is also equally applicable to any hydraulic cake-moulding machine. It regulates the number of cakes that can be made in any given time, and the attendant can only form a cake at such intervals as may be determined by the mill manager, thus ensuring that the meal shall be *evenly mixed, uniformly heated, and regularly distributed* to the presses. *Inter alia*, there are a very great reduction in wear and tear of bagging, a better and more regular yield of oil at a lower working pressure, and the improved appearance of the finished cakes. This regularity is got by aid of a hydraulic control valve which allows the pressure to pass only at predetermined intervals. The valve is actuated by a worm and worm wheel from the kettle, upright or cross shaft, or from any other convenient shaft, and any desired variation of speed may be obtained by change wheels. This control apparatus can be applied to any existing moulding machine.

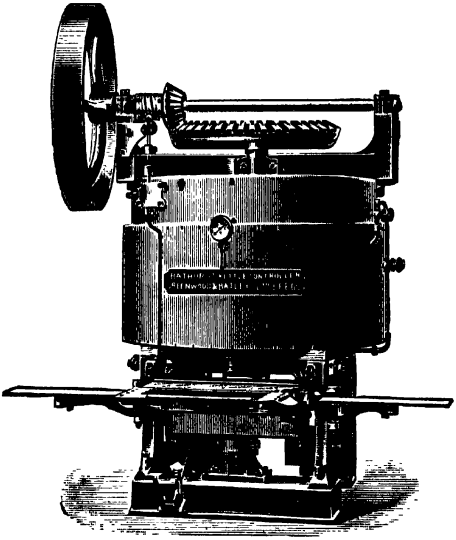


FIG. 26.—Bathurst kettle controller as applied to the patent self-acting seed kettle and cake-moulding machine.

Hydraulic Gauges.—Gauge, Fig. 27, of the most improved construction and fitted with maximum indicator, with lock-up, including piping and fittings connecting the gauge with the press. A similar gauge to Fig. 27 is sometimes fitted with an alarm bell mounted on a polished board. The bell is intended to ring when a certain predetermined pressure has been reached. The bell contains a clock movement, which is wound up by turning the knob on the top of the bell, and is set in action by a set of rods connected with the spring of the pressure gauge. The pressure at which the alarm shall

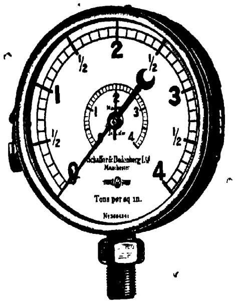


FIG. 27.—Hydraulic gauge.

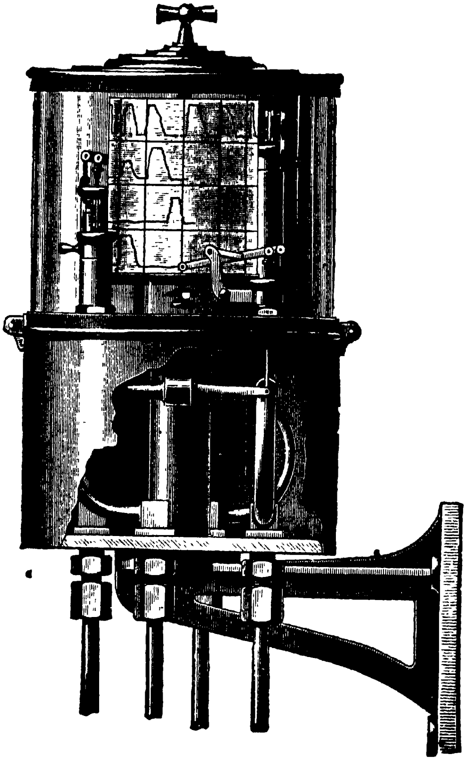


FIG. 28.—Mechanical recorder.

be given is arranged by setting an index pointer to the desired pressure on the scale, the pointer being secured to the vertical rod in the desired position by means ot two small milled nuts. The action of this apparatus is very reliable, and it can be confidently recommended.

The Automatic Mechanical Control of Oil-seed Crushing. Greenwood & Batley's Automatic Recorder.

Description.—This apparatus is designed to give a continuous record, in the form of a diagram, of the work performed by a system of hydraulic presses in the course of an interval of 12 or 24 hours. The diagram serves to show: (1) The times when the several presses were brought into action. (2) The rate of increase of pressure and the time occupied in attaining the maximum pressure. (3) The amount of the maximum pressure, and the length of time during

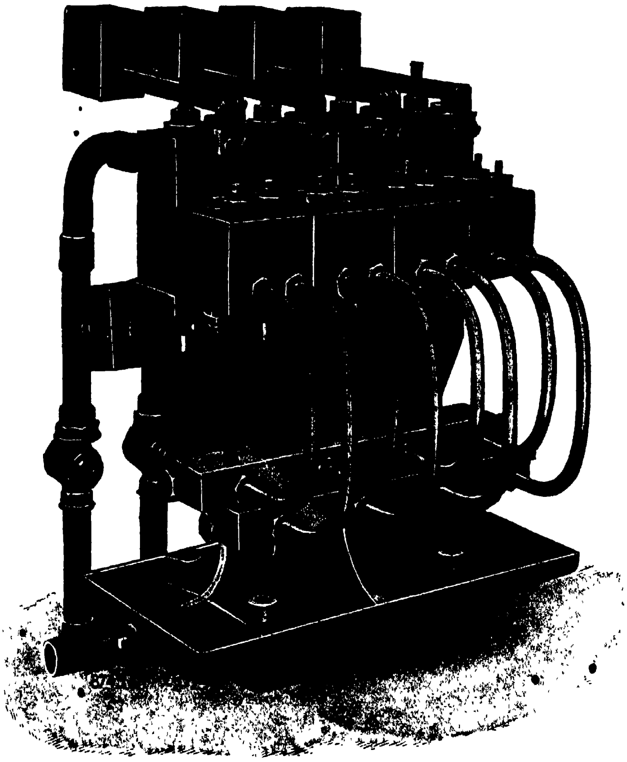


FIG. 29.—Group of four "Ideal" valves on cast-iron stand, showing pipe connections.

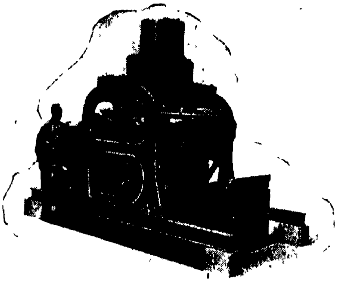
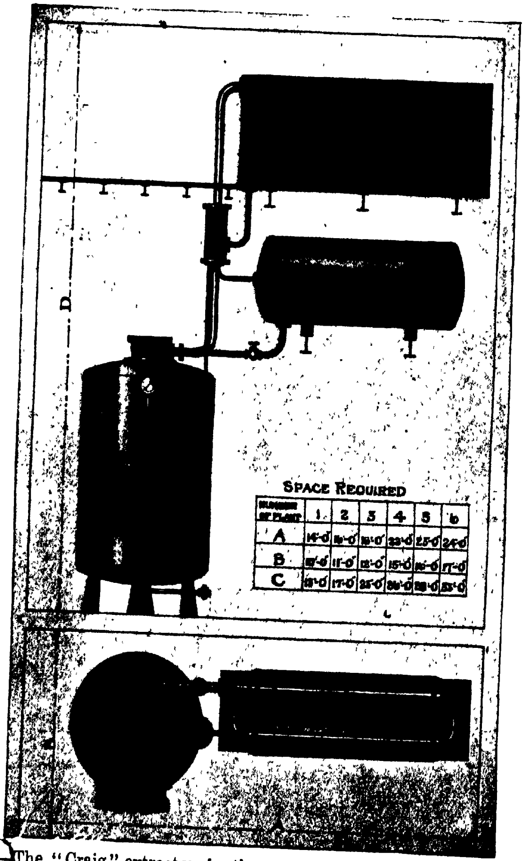


FIG. 30.—Oil weighing machine.



SPACE REQUIRED

NUMBER OF PLANT	1	2	3	4	5	6
A	14'-0"	[illegible]	[illegible]	[illegible]	25'-0"	24'-0"
B	[illegible]	11'-0"	[illegible]	15'-0"	[illegible]	17'-0"
C	[illegible]	17'-0"	25'-0"	[illegible]	[illegible]	[illegible]

FIG. 31.—The "Craig" extractor, for the extraction of oils, fats, waxes, paraffin etc., by the solvent process.

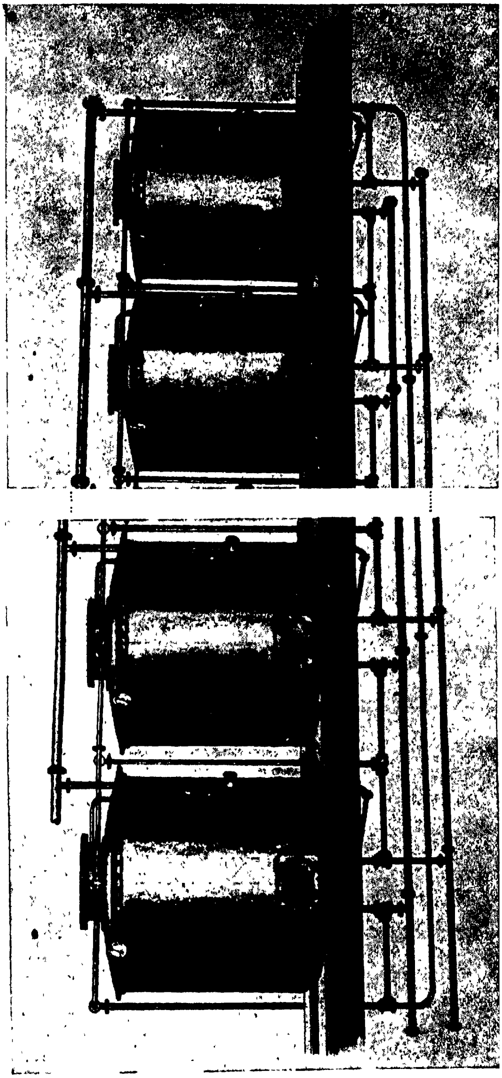


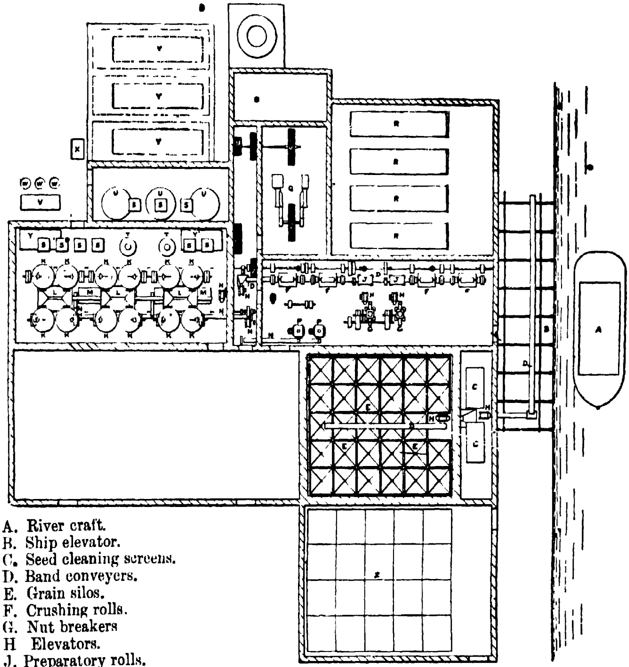
FIG. 32.—Zinc battery of extractors for extracting oil from seeds.

which this pressure was maintained. (4) The rate at which the pressure was reduced, and the time occupied in reducing the pressure. (5) The number of times the several presses were brought into operation, and the distribution of the work during different parts of the day or night. The apparatus is attached to a wall by means of a bracket, and the pipes projecting beneath the apparatus are connected to the cylinders of the presses. The pressure from each press enters a steel tube, which is constructed similar to those employed in high pressure gauges. The displacement of the end of the tube is transmitted to a parallel motion carrying a pencil, which marks the diagram on a slip of paper mounted upon a drum. This drum is rotated by clockwork at the rate of one revolution in 12 or 24 hours, the hours being marked by vertical lines on the diagram. The upper part of the apparatus is enclosed in a glass case, which can be opened and locked if required. The indicator is arranged to register the work of four presses simultaneously on the same slip of paper, the diagrams of the different presses being entirely independent. The apparatus is made very strong, the workmanship being of the highest excellence throughout.

Valves.—Ever since the introduction of accumulators into oil mills an automatic valve has been a desideratum. It is claimed that the "Ideal" valve supplies this want. The whole of the fittings are contained in a solid, forged, mild-steel block, and all are of special quality gun-metal or cast steel. The valve is entirely automatic in its action and does not in any way depend on the attention of the pressman, who only has to open the valve when he is ready to send the press ram up and close the valve when the press ram is to be lowered. When the admission valve is opened the low pressure flows through a regulating valve at full bore until the slack in the press is taken up, at which time the resistance in the press gradually closes this regulating valve, thus reducing the speed of the rise of the ram and saving wear and tear of bagging. This valve, however, does not quite close and consequently the pressure creeps on until the maximum pressure of the low pressure accumulator is reached, when the high pressure valve is automatically opened and the low pressure service is cut off by a check valve. The flow of the high pressure is also regulated by suitable means to prevent a too rapid rise of the ram. When the pressure has been on the press for the desired length of time, the admission valve is closed and the press ram falls. Special stop valves are supplied in each main valve so that the valves may be ground in when necessary without any other press out of action. The "Ideal" valve is simple and efficient and is not likely to get out of order, and once adjusted is always adjusted and certain in its action, and its makers claim for it a maximum yield of oil and a minimum wear and tear of press cloths. The system can also be applied to presses working with three pressures, such valves being chiefly used in connection with cage presses.

Extraction of Linseed Oil from the Seed by Solvents.—As linseed does not lend itself kindly to extraction by solvents, the process is not of importance; those interested will obtain full particulars in Andés' "Vegetable Oils" (Scott, Greenwood & Son); in addition Figs. 31, 32, 33, are shown, illustrating character of plant employed.

The main reason why linseed is not submitted to extraction is due to the fact that the residual meal would be devoid of oil content.



A. River craft.
B. Ship elevator.
C. Seed cleaning screens.
D. Band conveyers.
E. Grain silos.
F. Crushing rolls.
G. Nut breakers
H Elevators.
J. Preparatory rolls.
K. Extracting pots.
L. Bins.
M. Drying machines.
N. Screw conveyors.
P. Pulverators and weighing machines.
Q Engine.
R. Boilers.
S. Condensers.

T. Vacuum oil separators.
U. Evaporating stills.
V & W. Dephlegmator plant.
X. Solvent trap tank.
Y. Solvent stores.
Y^1. Mixed solvent tanks.
Z. Oil store tank.

Fig. 33.—Ground plan of solvent extraction plant to treat 600 tons per week.

Extractive methods, however, are employed in the laboratory, for in organised mills it is reasonable that each delivery of linseed should be regularly sampled and the percentage of oil ascertained by means of some such apparatus as shown in Figs. 34, 35, 36, the working of which is illustrated by Fig. 34 and explained as follows:—

The solvent distilled from B ascends tube A into condenser K, from which it falls on to a weighed amount of material to be

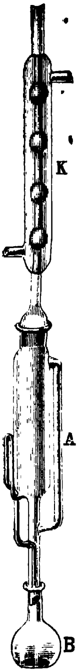


FIG. 34.—Oil extractor.

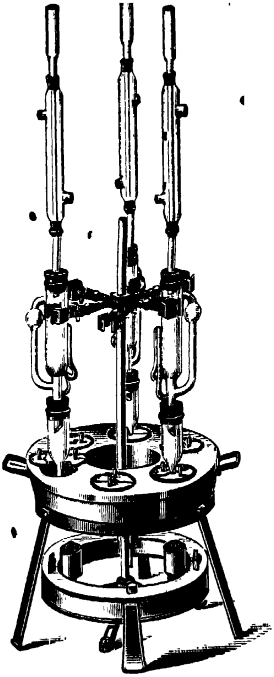


FIG. 35.—Battery of oil extractors being heated on water-bath.

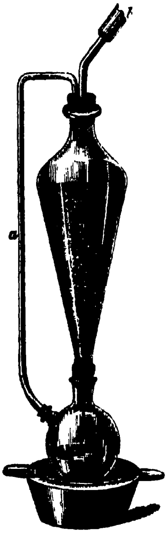


FIG. 36.—Fat extractor.

extracted, enclosed in a "thimble" of bibulous filter paper, or in its absence in fine wire gauze, and laid in the wide central tube of A, from which, charged with oil, it runs off automatically through left syphon tube into B, whence it is redistilled, and so the cycle goes on until the material is exhausted of oil, when the flask is detached, the ether distilled off, and the residual oil weighed.

By such means determination of the oil content of cake from the different presses would also be made, hence avoiding production of unsaleable cake caused through want of correct oil percentage guaranteed by vendors. Example: If an oil miller purchases 1000 tons of linseed containing 35 per cent. of oil, and he guarantees his cake to contain, say, 13·3 per cent. of oil, when stocktaking he should be able to account for 250 tons of oil and 750 tons of cake of above oil content. The following table gives percentage of oil obtainable by extractive methods from different seeds, etc., also percentage of oil in cakes.:—

PERCENTAGE OF OILS IN DIFFERENT SEEDS, ETC.

100 Parts of Each.	Oil per Cent.
Walnuts	40 to 70
Castor oil seeds	62
Hazel nuts	60
Garden cress seed	56 to 58
Sweet almonds	40 ,, 54
Bittor ,,	28 ,, 46
Poppy seeds	56 ,, 63
Oily radish seed	50
Sesamum (jugoline)	50
Lime-tree seeds	48
Cabbage seed	30 to 39
White mustard	36 ,, 38
Rape, Colewort, and Swedish Turnip seeds	33·5
Plum kernels	33·3
Colza seed	36 to 40
Rape ,,	30 ,, 36
Euphorbium (spurge seed)	30
Wild mustard seed	30
Camelina seed	28
Weld seed	29 to 36
Gourd ,,	25
Lemon ,,	25
Onocardium *acanthe*, or bear's foot	25
Hemp seed	14 to 25
Linseed	35 ,, 45
Black mustard seed	15
Beech mast	15 to 17
Sunflower seed	15
Stramonium, or thorn-apple seeds	15
Grapestones	14 to 22
Horsechestnuts	1·2 ,, 8
St. Julian plum	18

To obtain the above proportions of oil, the fruits must be all of good quality, deprived of their pods, coats, or *involucra*, and of all the parts destitute of oil, which also must be extracted in the best manner.

PERCENTAGE AND RATIOS OF OIL AND FREE FATTY ACIDS IN OIL SEEDS AND IN OILCAKES.

	Seeds.			Cakes.		
	100 Parts of Seed contain:		100 Parts of the Total Oil contains Fatty Acids.	Fatty Acid in Cake. Per Cent.	Total Oil in Cake. Per Cent.	Free Fatty Acid in Oil. Per Cent.
	Free Fatty Acids.	Total Oil.				
Rape seed . .	0·42	37·75	1·10	0·93	8·81	10·55
Kohl Rabi seed .	0·32	41·22	0·77	—	—	—
Poppy seed . .	3·20	46·90	6·66	5·66	9·63	58·89
Earth nut kernel .	1·91	46·09	4·15	1·42	7·65	18·62
,, husk .	1·91	4·43	43·10	—	—	—
Sesame . .	2·21	51·59	4·59	6·15	15·44	40·29
Palm kernel, with 6 per cent. husk	4·19	49·16	8·53	1·47	10·39	14·28
Koprah . .	2·98	67·40	4·42	1·31	18·11	10·51
Castor . . .	1·21	46·32	2·52	1·27	6·53	20·07
Linseed . .	—	—	—	0·75	8·81	9·75

CHAPTER III.

COMPOSITION OF LINSEED OIL—MUCILAGE OR FOOTS.

FRESHLY crushed raw linseed oil, or even oil that has *not* been tanked for some considerable time and has thus earned the distinction of old tanked oil, in other words, oil that has not been allowed to settle out by direct deposition, not only its suspended matter but also the impurities which it holds in solution, undergoes a change when heated to 400° F., a change by which the previously clear yellow becomes turbid. This change the oil boiler or varnish-maker describes as "breaking" or "spawning". Gelatinous transparent flakes appear in the oil about the size of herring scales. Although they eventually aggregate together into masses slightly darker in colour than the raw oil, none the less the removal of this break or spawn from the oil by filtration is exceedingly difficult. But the flakes at the moment at which they separate from the oil are colourless, clear, and transparent as the most colourless mica flakes, and it is said to be a characteristic of Baltic linseed oil that when heated to the breaking-point it assumes a beautiful blue colour, which the author has observed in many cases, but whether all such were Baltic oils he is not prepared to say. In any case, the blue colour is only transient and is much paler than the previous yellow colour. There is no doubt that the oil under the action of heat throws out colourless mucilage, and the colouring principle of the oil is carried down therewith as foots. Foots do not by any manner of means consist of the break nor of mucilage pure and simple. The volume or bulk of the break gives one the idea that the proportion of mucilage in the oil is somewhat large, but the actual weight present is very small. Thompson heated 2½ kilogrammes of linseed to breaking-point. The oil was cooled and filtered. As the precipitate clogged the filter it was removed to a glass where it was washed with petroleum ether by decantation. The non-oleaginous residue weighed 6·93 grammes = 0·277 per cent. of original oil. On ignition a portion of this residue gave 47·79 per cent. ash = 0·1177 per cent. of original oil. The oil filtered from break contained 0·0039 per cent. ash.

ANALYSIS OF ASH FROM "BREAK" OF LINSEED OIL.

	Per Cent.
CaO	20·96
MgO	18·54
P_2O_5	59·85
SO_3	trace
Total	99·35

The ash from the "break" contains P_2O_5, an excess of what would form an orthophosphate with the bases present. The oxygen in the P_2O_5 is to the oxygen in the bases in the ratio of 5 to 2, corresponding closely to that required by a pyrophosphate.

TABLE SHOWING ASH PER CENT. IN VARIOUS SAMPLES OF AMERICAN LINSEED OIL.

SAMPLES.			
1.	2.	3.	4.
Per Cent.	Per Cent.	Per Cent.	Per Cent.
0·1429	0·1967	0·0609	trace

1. Freshly double filtered raw American linseed oil.
2. Freshly double filtered raw American linseed oil.
3. Good well settled raw American linseed oil.
4. Best American varnish oil.

ANALYSIS OF ASH FROM SAMPLE 1.

	Per Cent. of the Oil.
CaO	0·0235
MgO	0·0221
P_2O_5	0·0705
K_2O	0·0043
SO_3	0·0027

Here again the P_2O_5 is in excess of bases and present largely in pyroform. Thompson quotes Mulder as speaking of the presence of $CaSO_4$ in linseed oil (but that has been shown to be quite wrong). No one, says Thompson, had hitherto mentioned the presence of phosphates. To locate origin of ingredients of linseed oil ash, Thompson analysed the ash from American flax seed and the linseed oil cake made therefrom.

TABLE SHOWING PERCENTAGE OF ASH IN AMERICAN LINSEED AND IN THE LINSEED OILCAKE MADE THEREFROM. (THOMPSON.)

	Linseed. Per Cent.	Oilcake. Per Cent.
Ash	3·112	4·899
N_2O_2	1·83	1·51
$Fe_2O_3Al_2O_3$	1·25	1·59
CaO	9·46	9·24
MgO	18·31	18·52
K_2O	26·18	26·14
Na_2O	1·71	3·59
SO_3	3·96	3·51
P_2O_5	35·44	36·28

These analyses confirm previous ones. If the ratio between the oxygen and the bases and the oxygen in the phosphoric anhydride in an orthophosphate be as 3 to 5, then the bases are here in excess. The P_2O_5, CaO, MgO are dissolved to some extent by the oil. Very little of the chief base potash is taken up by the oil. Schmidt, Kirchner, and Tollans reported phosphates in the mucilage from linseed. These phosphates in linseed are probably largely combined with mucilage, and the compound so formed dissolved to some extent by the oil. This requires confirmation. Thompson examined a portion of thoroughly extracted break for mucilage and obtained no reaction. The break was heated with dilute HCl for a few seconds, cooled and filtered, and alcohol added. No precipitate was obtained. It may have been, says Thompson, that the mucilage was decomposed at the temperature applied. Thompson tested for albumenoids in linseed oil and found nitrogen less than 0·01 per cent. The same sample showed 0·04 P. This points to the phosphates being comparatively much greater than nitrogenous matter. A portion of extracted break showed some N, although less than 1 per cent. of the "break". The P, on the other hand, amounted to 9·60 per cent. of the break = 57 per cent. of ash in break.

Mucilage is therefore a normal ingredient of raw oil which from a technical point of view is generally regarded as an impurity. Moreover, unripe wet seed yields an oil rich in mucilage. Linseed oil which has passed through a filter press contains little mucilage. In many factories it is filtered through cloth filters, and the mucilage retained is mixed warm with the next batch of freshly cleaned seed and pressed. The oil so obtained is rich in mucilage. When linseed oil is stored in a tank it deposits a large amount of mucilage as foots, part of that dissolved by the oil. Mucilage is not a simple body, it varies with the different substances present in the seed which during the process of oil crushing pass into the oil. The amount varies under whatever circumstances but very little. However, linseed oil may be clear and bright and yet contain mucilage. When such an oil is rapidly heated to 250° to 300° C. (482° to 572° F.) the mucilage separates out in flakes (the oil often assumes a bluish-green coloration). The foots occupy a large space and there seems a great weight of them; they are extraordinary bulky so that their actual weight turns out very small. Mucilage appears during the conversion of linseed oil into boiled oil so that its removal is desirable. Mucilage-freed oil is termed "varnish oil". Instead of removing the mucilage by heat, attempts have been made to precipitate the mucilage by cooling. G. Bentz exposed mucilaginous oil to a temperature of about – 4° C. for about 24 hours, and on again warming the oil so treated only quite a small quantity of the separated mucilage again dissolved in the oil. According to Niegemann this conclusion regarding linseed does not agree with his own researches, in which it dissolves during the separation of the unsaponifiable. It is therefore absent. The unsaponifiable content of linseed oil is a homogeneous waxy mass soluble in hot alcohol. Bomer crystallised the unsaponifiable from linseed oil, three to six times from hot alcohol, and thus obtained colourless monoclinic crystals of phytosterin, m.p. 137·5 to 138° C. The variations in the properties of phytosterin are accounted for by the fact that various vegetable oils, in addition to phytosterin contain other alcohols of high molecular weight, also carbides in small quantity. Niegemann's statement that linseed oil unsaponifiable contains unsaturated albumenoid bodies is unfounded, as during saponification these would be resolved into substances insoluble both in ether and petroleum ether. Researches have shown that linseed oil cooled to near its freezing-point—viz. to about − 20° C.—and then filtered at a little higher temperature, was always below 0° C. The linseed oil so treated was no longer turbid, and the precipitated mucilage was oil-free. Fraine heated linseed oil with a small quantity of ground quicklime, but according to Niegemann the oil so treated darkens on subsequent heating. Stelling prepared a special filter in which the mucilage was subjected to catalytic action: it was first treated with a solution of nitrate of manganese, then with a solution of borax. Fuller's earth has been used to free linseed oil from mucilage. The oil is filtered through a deep layer of the coarse earth or it is intimately mixed with the finely pulverised earth and passed through a filter press. That the mucilage is completely removed in this way is somewhat doubtful. Liebig was familiar with linseed oil mucilage and believed it to hinder the drying of the oil. On prolonged storage, heating with metallic oxides removed it. On his direct instructions the oil was treated with lead acetate. Mulder denied that mucilage occurs in good linseed oil.

Cold pressed linseed oil passes turbid from the press, but it clarifies on standing, filtration, or treatment with chemical reagents. That warm pressed linseed oil can dissolve albumen can hardly be, as it would coagulate at the temperature used. Plant mucilage would become dry and insoluble. Mulder treated a hot pressed oil with lead acetate, and so obtained a very oily deposit in which he found no mucilage, only lead soap and lead carbonate. Weger remarks that Mulder must have used a specially good sample of linseed oil, also that his method of identifying the mucilage was defective as it may be present in perfectly clear oil. By treating oil with wood charcoal the dissolved mucilage is removed. On prolonged heating of the oil the mucilage separates out. Weger filtered off the mucilage separated by heat and tried to free it from oil by keeping it on porous tiles, but did not do so completely. It then formed a gelatinous transparent mass, with a thick surface layer in a few days. Such a mucilage shows a refraction of 77·5 against 72·4 for the oil not freed from mucilage. Linseed oil mucilage must not be confused with linseed mucilage obtained by extracting linseed with ether and precipitating the aqueous extract with alcohol. The mucilage so obtained contains many mineral substances, especially phosphates of lime and magnesia, also SiO_2, SO_3, Cl, K, Na. The organic portion contains no starch nor traces of cellulose nor leaves sugar on hydrolysis with dilute acids. G. W. Thompson made several examinations of linseed oil mucilage. He heated the fresh expressed oil to 400° F., filtered the gelatinous precipitate, and washed it free from its contained oil by petroleum ether. The insoluble residue formed 0·277 per cent. of the linseed oil. It contained 47·79 per cent. of ash, chiefly CaO, MgO, P_2O_5. However, C. Niegemann believes that linseed mucilage consists in greater part of an albuminous body. Extracted at 120° C. on filtration it is pure white; its solution in acetic acid gives with concentrated sulphuric acid the characteristic violet reaction of albuminous bodies. Kochs heated fresh linseed oil, let it settle, and treated the precipitate obtained with ether. His amount was only 0·06 of the weight of the oil, which was greyish-white. It had a faint smell of trimethylamine which became stronger on heating, showing signs of a decomposing albuminous body. Under the microscope mycelium, spores, mucilagenous algæ, dust particles, fibrous particles, hair fragments, etc., were noted. On treatment with dilute HCl the substance reduced Fehling's solution, due to a carbohydrate. From the Cu found a linseed mucilage of 16·3 per cent. was calculated. On a second experiment with Indian linseed only 0·009 per cent. of an apparently solid precipitate was obtained from which 11·3 per cent. of an albuminous body was calculated from the N content, 9·1 per cent. ash, and about 80 per cent. of linoxin. Eisenschiml and Copthorne found a separation of mucilage in the foots from expressed oil and from naphtha extracted oil. Whilst the ash of the first consists in greater part of CaO, MgO, P_2O_5, it is free from silica, and that from the extracted oil on one occasion showed as much as 34·8 per cent. Whilst the inorganic portion of linseed oil mucilage appears to be the same as that from linseed, it is not so with the organic portion. For the elucidation of this point further research is necessary. The aqueous alcoholic strongly alkaline solution is extracted by petroleum ether. The method was chiefly used by Honig and Spitz.

For the correct estimation of the unsaponifiable content in linseed oil, the following method is adopted. About 10 grammes of linseed oil, accurately weighed, are saponified by 40 c.c. double normal alcoholic potash, the dried soap dissolved in 100 c.c. 50 per cent. alcohol, and the solution run quantitatively into a separating funnel. On cooling, it is shaken once with 100 c.c. petroleum ether, and four times with 50 c.c. petroleum ether. The layers thus form very rapidly, so that each extraction only averages half an hour, and then the alcoholic aqueous solution is run off. The different petroleum ether extracts are run into a second separating funnel, so as to remove any entrained soap, by washing with 20 c.c. of 50 per cent. alcohol, with which it is treated for half an hour. The greater part of the petroleum ether is distilled off the residue with the addition of petroleum ether, is run into a porcelain basin, and dried as usual on the water-bath. Honig and Spitz have also given a rapid method, the results of which are technically accurate, as the petroleum ether only absorbs a minimum of soap. They use a special flask in the following process into which the top layer is run. The dried soap from about 5 grammes

Allen found the following percentages of unsaponifiable matter in various oils:—

Oil.	Per Cent.	Oil.	Per Cent.
Olive	1·14	Sperm	41·49
Rape	1·0	Spermaceti	49·68
Castor	0·71	Japan wax	1·14
Cod liver	1·82	Lard	0·23
Palm	0·54	Cocoa-butter	0·22
Butter	0·46		

Fahrion has compiled the following table of the different results of different observers in the determination of the unsaponifiable matter in linseed oil:—

Authority.	Year.	Unsaponifiable. Per Cent.	Iodine No	Remarks.
Thompson and Ballantyne	1891	1·09 – 1·28	—	—
R. Williams	1895	0·8 – 1·3	—	—
O. Bach	1898	0·32 – 0·90	—	—
Lewkowitsch	1898	0·6 – 1·1	—	—
Niegemann	1904	0·74 – 2·15	59·2 – 91·2	Method 1 without purification results 25 per cent too high
Thoms and Fendler	1904	0·97 – 1·25	83·2 – 97·0	Method 4
Thompson and Dunlop	1906	0·88 – 1·25	—	—
Fahrion	1907	0·92	83·5	Method 2
"	"	0·97	90·0	" 3
"	"	0·97	82·6	" 4

Fahrion believes, particularly in the separation of mineral oils from fatty oils, that not the alkaline but the neutral alcoholic solution should be extracted with petroleum ether, because using 50 per cent. alcohol, no dissociation of the soap occurs. Such a supposition is in conflict with that of D. Holde, who holds that, with every new shaking with petroleum ether slight dissociation of the soap occurs, which is first prevented by the use of 80 per cent. alcohol. Fahrion's modification gives high results. In commercial oleins the difference may be 1 per cent. and more. With linseed oil, however, it is very small, on one occasion only 0·05 per cent.

During shaking with petroleum ether it is found that phytosterin dissolves with difficulty in that solvent. It is much more soluble in ether. A method first described by Bomer, and altered in certain points by Fendler, is described below: 10 grammes of oil are saponified in a flask with reflux condenser, with 20 c.c. of a solution of 200 grammes of caustic potash in a litre of alcohol of 70° F., the soap solution run into a separating funnel, and diluted with 40 c.c. water, so that it will contain 20 per cent. alcohol. It is (1) first extracted with 100 then (2) with 50 c.c. of ether. The different ether extracts are washed with water.

"The Determination of Unsaponifiable Matter in Oils, Fats, and Waxes" has been the object of some remarks by John M. Wilkie, B.Sc., F.I.C. This determination is often troublesome owing to emulsification. By adopting a definite concentration of alcohol and ether before extraction, best obtained by the use of $n/2$ alcoholic KOH for hydrolysis, the formation of emulsions may be entirely prevented, and the determination finished in 30 minutes after saponification. The trouble experienced in the analysis of bees' and other waxes, lanoline, etc., may be entirely eliminated by using 0·5 gramme of wax and 4·5 grammes of castor oil, extracting as usual, and making a correction for the unsaponifiable matter in the castor oil.

Phytosterin and Cholesterin.—Oils and fats contain in small quantity unsaponifiable principles, soluble in ether, very slightly soluble in cold alcohol and soluble in boiling alcohol. As the unsaponifiable principle which characterises vegetable oils, phytosterin, discovered by Hesse in oil of Calabar beans, differs very essentially from the unsaponifiable principle of animal oils, cholesterin, the two substances may be used in a comparative manner to detect, say, fish oil in linseed oil or, vice versa, cotton-seed oil in lard oil. Both have the same chemical composition, $C_{27}H_{46}O$, and are said to have the same constitution, but that is not as yet sufficiently clear. Cholesterin is chiefly found in liver oils. To isolate these principles Salkowski saponifies 50 grammes of fat, dissolves the soap in 2 litres of water, and shakes up the soap solution repeatedly with ether. By evaporation the ethereal solution yields a crystalline residue which after being purified by cold alcohol is examined under the microscope.

Cholesterin crystallises in thin rhombic plates, melts at 146° C. = 294·8° F. Phytosterin yields stellate crystals or a mass of long rigid needles. It melts at 132° C. (269·6 F.). The residue left by the evaporation of the ether is then dissolved in a little chloroform and 20 drops of acetic anhydride and concentrated sulphuric acid are added. Cholesterin develops a cherry-red coloration, whilst phytosterin gives a bluish-red with a green fluorescence bloom. When cholesterin is mixed with its homologue phytosterin, it masks the reactions of the latter and the melting-point is lowered to less than 146° C. (294·8° F.). Windaus gives the following particulars regarding cholesterol. It is an unsaturated secondary alcohol. The hydroxyl is enclosed in a hydrogen ring between two methylen groups. The double bonds are enclosed in an end-placed vinyl group $CH : CH_2$. The molecule finally contains an isopropyl group and four hydrogen rings. It is a complex terpene which closely resembles cholic acid.

Phytosterin is not regarded as a pure substance but as mixed with other as yet unknown bodies. The mixture constitutes the unsaponifiable. Glycerine is also unsaponifiable but is readily soluble in water.

Lezithin is also a tri-glyceride, in which the fatty acids are partially replaced by other acids. It yields on saponification, fatty acids, glycerine phosphate, $C_3H_5(OH)_3(PO_4H_2)$, and cholin,

$$C_2H_4(OH).N(CH_3)_3OH.$$

Schulze and Stigger found 0·8 per cent. lezithin in linseed, and it appears that a considerable proportion passes into the oil during oil-crushing. H. Jaecke found in the latter 0·33 per cent. more than in any other vegetable oil. He believes it to be combined, in the seed, with an albuminous body, which substance, during oil-crushing, is partially decomposed. He estimates its amount readily from the P. content of ash. E. Schulze has shown how it is extracted from the oil and isolated therefrom.

Colour Test for Cholesterin.—If cholesterin be moistened by hydrochloric acid or sulphuric acid containing Fe_2Cl_6 it becomes of a magnificent violet colour. A mixture of two or three volumes of concentrated hydrochloric or sulphuric acid and one of a dilute solution of the perchloride will do for the test, or even the commercial hydrochloric acid. A small particle of cholesterin should be rubbed by a glass rod with a drop of the reagent and the mixture then gently warmed. It first becomes of a reddish colour which as the temperature rises changes to a blue-violet colour; strong heat destroys the colour. When sulphuric acid is used the mixture must be warmed more cautiously. It first becomes carmine-red, then violet, and at a high temperature is carbonised. Nitric acid and phosphoric acid with the perchloride will not give the reaction.

Liebermann's Cholesterol Reaction.—0·001 to 0·003 gramme substance are dissolved in 10 drops of acetic anhydride, and 1 to 2 drops of concentrated sulphuric acid added in the cold. The colour depends on the quantity of substance and the temperature.

Phytosterin as greasy plates—red, violet, blue, green.

Isocholesterin—red, yellow.

Water.—Raw linseed oil may be perfectly clear and yet contain up to 0·3 per cent. American and Russian oil are richer in water than Indian. On heating oil containing water the water is removed as steam bubbles about 120° to 130° C., which point many still call the "boiling-point" of linseed oil. Linseed oil may be freed from contained water by filtration through fuller's earth (see p. 46). In America the effect of hot pressing on the oil is regarded as negligible, as is also the amount of moisture present in or added to the seeds to facilitate pressing and to form coherent cakes. In many seasons no moisture whatever is added to the oil.

The ash content of linseed oil is usually very small. Mulder found 0·03 per cent. Mucilaginous linseed oil contains more ash than mucilage-free oil. Thompson found in American raw oils up to 0·20 per cent. ash, chiefly MgO, CaO, P_2O_5. In refined oil only traces. The American Committee on Testing Materials give the ash content from 0·02 up to 0·16 per cent.

CHAPTER IV.

REFINING AND BLEACHING LINSEED OIL.

Oil Refining.—The oil expressed from oil seeds, or extracted therefrom by solvents, is very impure; and owing to the presence of easily decomposable foreign substances, amongst which albumenoid substances predominate, and *inter alia* contain enzymes which start the decay of the oil, paint, or varnish into which they enter, linseed oil should not be used in its raw unrefined pristine condition. Be it well understood that the raw oil is used in contradistinction to boiled oil and in no other sense. Raw oil should therefore be refined.

Mechanical Purification of Oil by Filters.—The *first* stage of the refining process is *mechanical*, the *second*, *chemical*. The oil is purified *mechanically* by conveying it as it comes from the presses into a reservoir, from whence a pump distributes it to the filter presses, in which the greater part of the impurities which it holds in suspension are separated. The dissolved impurities, including dissolved mucilage, pass through the filter, still in solution.

Chemical Purification—Refining.—*Chemical* purification consists in treating the oil, *after it has been previously mechanically clarified*, in a methodical manner with dehydrating agents such as concentrated sulphuric acid and certain salts.

By Acids: Thenard's Process of Charring the Mucilage without Charring the Oil.—By using a quantity of not too strong sulphuric acid (1 to 1½ per cent. of 168° Tw.; specific gravity 1·84), the acid exerts its action on the foreign matters contained in the oil in preference to the oil itself—it acts at first by absorbing moisture; it then attacks the foreign matters and transforms them into a carbonaceous mass, which imparts to the oil a brown coloration, which quickly deposits as a flocculent precipitate. When the acid has completely charred these substances, water is turned on to dilute the acid, so as to prevent it acting on the oil. After being energetically agitated with injection of air, and repeated washing with water heated by an open steam pipe, the oil is conveyed into large tanks and left to settle. It only remains to separate the purified oil by decantation. According to Hartley, however, oil treated in this manner is itself frequently charred, or retains some impurity which, dissolving in the oil, imparts thereto a brown coloration, which is not removed by the subsequent bleaching process to which the natural colouring

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be superfluous to dwell longer upon these different processes. This short enumeration will be sufficient. The purified oil is then stored in large reservoirs.

Cogan's Method of Refining Linseed Oil.—Cogan's process, although similar to Thenard's in the first part of it, differs therefrom in the latter part by the judicious introduction of steam, by aid of which the oil is almost entirely freed from acid and the black mucilaginous dregs subside in the course of twelve hours, leaving the upper portion of the oil quite clear and greatly improved in colour, and in those qualities for which it is esteemed by the painter. Cogan operated on 100 gallons at a time, using for that amount 3 quarts or 10 lb. of concentrated sulphuric acid. These 3 quarts of acid he diluted with an equal bulk of water, that is, with 3 quarts. The oil being run into a copper pan of the shape of a boiler, 2 quarts of the dilute acid are to be added; the whole is then to be stirred up very carefully for an hour or more with a wooden scoop till the acid is completely incorporated with the oil and the colour of the latter has become much deeper than at first. A second similar quantity of acid is to be added and mixed with the oil in the same way as the first was, and then the remaining part of the acid is to be added. The stirring of the oil is continued altogether, at the end of which the colour of the mixture will be nearly that of tar. It is then to be allowed to stand quiet for a night and in the morning is to be transferred to the boiler. This is of copper, and has a steam pipe entering it at the bottom and then dividing into three or four branches, each of which terminates in a perforated plate. The steam thus thrown in passes in a very finely divided state into the oil, penetrates into every part of it, and heats it to the temperature of boiling water. The steaming process is to be continued for 6 or 7 hours, at the end of which time it is to be transferred to a cooler of the form of an inverted cone, terminating in a short pipe commanded by a stop-cock and also having a stop-cock inserted in its side a few inches from the bottom. After remaining a night in the cooler, the oil is fit to be withdrawn. For this purpose the cock at the bottom is opened and the black watery acid liquor flows out. As soon as the oil begins to come the cock is closed and that in the side of the cooler is opened. From this the oil runs quite clear and limpid, the whole of that which is still turbid remaining below the upper cock. The purified oil being drawn off, that which is still turbid remains below the upper cock. The purified oil being drawn off, that which is turbid is let out into a reservoir, where it either remains to clarify by subsidence or is mixed with the next portion of raw oil; 1 per cent. of linoleate of manganese, dissolved in rectified coal tar naphtha, can now be added to the oil and the mixture of oil and liquid drier will form a clear solution with the oil. Lead driers—lead rosinate, lead linoleate, etc.—should never be added to oil intended to be used as a vehicle and binding agent for zinc oxide and white zinc paints generally, more especially with paints containing zinc sulphide, as it turns the paint grey from the formation of black lead sulphide. Again, all the virtue of using a zinc white pigment and the care taken in refining the oil is to a large extent lost if a plumbiferous zinc oxide be used.

Bleaching of Linseed Oil.—For high-class varnishes and high-class paints and enamels it is necessary to use a very pale oil. Even with an oil which only shows a very faint yellow tint the quality of the varnish into which it enters will be deteriorated. It is therefore necessary to bleach the oil.

The Nature of the Colouring Principles of Oil.—The colouring principles of oils are derived from powerful colouring matters existing in the fruits and seeds from whence they have been extracted. They are identical with the colouring matter present in the leaves of plants. They may be resolved into four principal substances of very similar chemical composition· Xanthophyll and chlorophyll, both yellow, another, but blue, chlorophyll, and finally erythrophyll, of a red colour. These substances are not necessarily found in *all* oils, but nevertheless they are always present in linseed oil, and the variations in their relative proportions are the cause of the different colours which different samples of crude raw unrefined linseed oil exhibit. If erythrophyll and a mixture of the two chlorophylls predominate we get a brown oil; if a greater proportion of chlorophyll be present the oil will have a greenish-brown tint; finally, if xanthophyll predominates a pale yellow oil is the result. These substances are decolorised by sunlight, especially in contact with air; oxidation also destroys them; they are also easily decolorised by dilute acids. Alkalies and certain metallic salts first precipitate the chlorophyll, then in the long run, if added in excess, the other two substances are likewise precipitated; finally, they are rapidly decolorised by chlorine and hypochlorites.

Five processes of bleaching oils are in use based upon the preceding remarks: (1) By sunlight alone, or by sunlight and air acting together; (2) by oxidising agents; (3) by acids; (4) by alkalies or metallic salts; (5) by chlorine.

1. *Action of Light in Bleaching of Linseed Oil.*—Be it well understood at the outset that the action of light as an accelerator of the drying of linseed oil is not dealt with in this paragraph. In decolorising oil the best result is obtained by the prolonged action of sunlight, and a superior article is said to be obtained to that yielded by the use of chemical reagents. This may be true of many chemicals, but not of oil refined by sulphuric acid. When linseed oil is exposed in a very thin layer to the direct action of sunlight, it bleaches in two hours. Working with large quantities the process is of course of longer duration, but by using large flasks of colourless glass, says Livache, and exposing the oil in these to direct sunlight, bleaching proceeds very rapidly, and so that the oxygen of the air may aid in the operation the mouths of the flasks are simply plugged

with cotton wool. When it is desired to treat larger quantities the oil is placed in flat lead-lined or zinc-lined boxes about 40 inches long by 20 inches wide and 6 to 10 inches deep, covered with a glass plate, and slightly inclined by raising one of the sides of the box about ½ inch or so; or the glass plate is made to overlap the sides of the box, so that no rain-water gains access to the contents of the boxes, which are generally placed in the open air. Finally, two tubes lead into the box from the two opposite sides, so that the air on the surface of the oil is being constantly renewed. Linseed oil, it is said, can thus be bleached to a bright colourless oil in less than a fortnight.

2. *By Oxidising Agents: (a) Peroxide of hydrogen*, which is now easily obtainable in commerce, has also been recommended. The oil is shaken with 5 to 10 per cent. of peroxide of hydrogen of 10 per cent. strength. This process would appear to be only adaptable to small quantities. Expense would debar its use on the large scale, and, as a matter of fact, quite irrespective of expense, both peroxides of hydrogen and sodium have no practical value as oil-bleaching agents, however energetic they ought to be theoretically in this respect, and it is only a waste of time, money, and patience to attempt to bleach oil in this way.

(*b*) *Ozone.*—Attempts have been made to use ozone. It is made by causing a current of air to pass through a series of ordinary ozonising tubes, where it becomes richer and richer in ozone, being finally led to a receiver containing the oil to be oxidised. The oil is heated by a steam coil to about 40° to 50° C., and the ozonised air is admitted to the bottom of the vessel, and is made to pass through the whole of the oil by means of a tube pierced with very small holes. Schrader and Dumcke found that ozone only acts upon the oil for a comparatively short time—it in fact stops very quickly. But if the oil thus treated be placed in white glass flasks in flat boxes, in contact with air and preferably in the sun, the action continues of its own accord, bleaching and thickening the oil in a very short time, and causing it to dry much more rapidly.

(*c*) *By Permanganate or Bichromate of Potash.*—The permanganate, or, better still, the bichromate of potash, in conjunction with sulphuric acid, have long been used as bleaching agents. The process is conducted in lead-lined wooden tanks. For every 100 lb. of oil about ¼ lb. of bichromate of potash is mixed with 1 lb. of sulphuric acid, previously diluted with ½ gallon of water. This mixture is run into the oil in a thin stream, with constant stirring, kept up for an hour, the oil, if need be, being heated all the time by a steam coil. The liquids are allowed to separate, the lower layer drawn off, and the oil repeatedly washed with hot water. This process is tedious, owing to the difficulty of eliminating even by acid the green hydrated oxide of chromium which dissolves in the oil. The same remark applies to bleaching with manganese compounds, where a similar hitch occurs. There is a great loss of oil in both processes, altogether incompatible with the extent, if any, to which the oil may be bleached. However, in both cases the oil may increase in drying properties owing to the action of the nascent oxygen developed in the processes in question. *By Linoleate of Manganese.*—Blenkinsop and Hartley proposed to bleach linseed oil, or rather to produce a "boiled" oil paler than "raw" oil, by oxide of manganese introduced in the state of linoleate of manganese dissolved in coal-tar naphtha. The process involves the use of heat. The oxygen used up in oxidising the oil and bleaching the colouring matters is restored to the manganese by a current of air as fast as it is deprived of it. But this process was well known both in Britain and America long before the date of this patent.

3. *By Acids: (a) By Nitric Acid, etc.*—Lawson has suggested dilute nitric acid. The process should be most carefully watched, so as to prevent any elevation of temperature. In England, according to Livache, use is made of a mixture of nitric acid and chlorate of potash in the proportion of 1 to 2 per cent. of the oil to be decolorised; heat is applied, and the oil is then repeatedly washed with water. This process, he says, has been successfully employed with cotton-seed oil, but as a matter of fact the caustic soda method for refining cotton-seed oil and the sulphuric acid method for refining linseed reign supreme in Britain, and this is in accordance with the fact that it is principally coloured *mucilaginous* impurities which have to be got rid of in refining linseed oil, whilst it is coloured *resinous* impurities which are present in crude cotton-seed oil.

(*b*) *Sulphuric Acid*, see p. 53.

4. *By Alkalies and Metallic Salts: (a) By Caustic Soda.*—Certain oils, containing resinous colouring principles, particularly cotton-seed oil, may be completely decolorised by agitation with a small quantity of *caustic potash* or *soda* (1 per cent.). Combination with the colouring principles ensues, and as a result these are precipitated as cotton-seed oil foots, from which the purified oil may be easily run off through a syphon or otherwise. It is not applicable to linseed oil —at least to the same extent. (*b*) *By Carbonate of Potash.*—5 lb. of the carbonate dissolved in 10 gallons of water are added to 100 lb. of oil, and the mixture stirred to thorough incorporation; 2½ gallons of a 2 per cent. solution of chloride of calcium are then added. The oil bleaches rapidly, and it is then decanted and treated with a 5 per cent. solution of sulphuric acid, and afterwards washed until perfectly neutral. But this would be far too laborious and expensive a process for adoption on the large scale, and like others has nothing to recommend it over the sulphuric acid process. (*c*) *By Ferrous Sulphate: Artists' Oil.*—Amongst the salts proposed, ferrous sulphate (green vitriol) is capable of giving good results, with small quantities of oil. *Process.*—One part of green vitriol is dissolved in 1½ parts of water, and this mixture is added to double its volume of linseed oil contained in a glass flask. The whole is then exposed to sunlight, and shaken

at least once a day. The oil is generally bleached in from three to six weeks, according to the amount of sunshine. When the oil is decanted the green vitriol solution can be used over again for treating a fresh quantity of oil. This process is much in vogue with artists' colourmen (the bleached oil being sold as *artists'* oil), but is too tedious, laborious and costly for adoption on the large scale. (*d*) *By Basic Acetate of Lead.*—A solution of basic acetate of lead when agitated with oil eliminates its colouring principles very effectually. (*e*) *By Lead Sulphate.*—This process also gives good results. It is mixed with oil to the consistency of cream, and exposed, with frequent agitation. After a time the oil is bleached. Two layers are found at the bottom of the flask, one consisting of lead sulphate, the other of colouring matter. The lead sulphate may be used over again. The rationale of the process is obscure. It may be looked upon as similar to the clarification of beer by isinglass. (*f*) *By Complex Mixtures.*—More or less complex mixtures of different metallic salts are also used. The following give good results: To 10 gallons of linseed oil are added 1½ gallons of water, containing ½ lb. of black oxide of manganese, ¼ lb. of bichromate, ¼ lb. of carbonate of soda, and ¼ lb. of common salt. The boiling solution is added to the oil; it is left to clarify, and the colourless oil decanted.

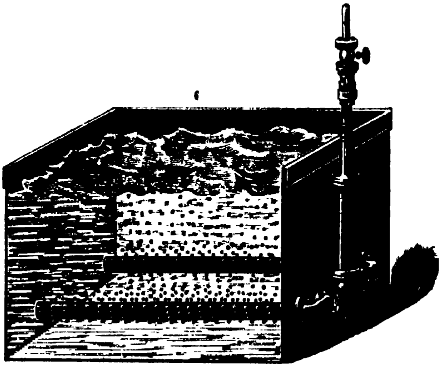


FIG. 37.—Apparatus for bleaching linseed oil by a current of air which has been passed over chloride of lime.

5. *By Chlorine.*—Substances from which chlorine can be generated without the aid of heat are added to the oil. For instance, 5 lb. of concentrated hydrochloric acid, 33 per cent., diluted with four times its weight of water, are added to 10 gallons of oil. The whole is well stirred, whilst a solution of 1 lb. of bichromate in 1 gallon of water is added. A mixture of red lead and hydrochloric acid may also be used. To 10 gallons of oil ½ lb. of red lead beaten up with

½ lb. of oil is added, and the whole well stirred, whilst ½ lb. of hydrochloric acid is added. During the next five days an additional ½ lb. of hydrochloric acid is added daily, the whole being well stirred several times during the 24 hours. The decanted oil is run into large bottles, or placed in boxes lined with lead, and exposed to sunlight until the oil is perfectly colourless.

The most rapid method of bleaching oils, it has been asserted, is by means of chemical reagents, especially chlorine, but it must not be forgotten that it is difficult to free the oil from all trace of these reagents, which in the end may exert a vexatious and injurious influence upon the final products manufactured from an oil bleached in this way. As a matter of fact, chlorine does not bleach linseed oil, it darkens it; and the chlorine test for fish oil is, in virtue of this darkening, a delusion and a snare. Certain bleaching agents, like chlorine and nitrous acid, are apt to form substitution compounds which alter altogether the nature of the oil, and not for the better. Had one space at his disposal, and a sufficient supply of refined oil to meet his wants in the meantime, says Livache, the bleaching of oil by means of sunlight in flat boxes covered with glass plates cannot be too highly recommended. The slowness of the process would, he says, be largely compensated by the beauty and quality of the products manufactured from such an oil.

However that may be, an equally good product can be obtained by bleaching with sulphuric acid in fewer hours than it takes weeks by sunlight. In fact, bleaching by sunlight could only be recommended by those who have never seen linseed oil efficiently refined by sulphuric acid, which is the most effectual, the most expeditious and the most economical process, requiring no costly plant, no costly chemicals, only about 1 lb. of oil of vitriol per 10 gallons of oil. A steam pipe heated by exhaust steam mixes the acid and oil together, and does all the agitation necessary for washing the acid out of the oil, all the operations being done in the one tank if need be. No process could be cheaper, no process could be more simple, but it requires care and experience, as it is quite easy for ultra-cocksure graduates in chemistry with the highest honours, to their own sorrow and the disgust of their employers, to irretreivably spoil 5 to 10 tons of oil which being permanently darkened can then only be used for very low grade boiled oil.

Mulder previously filtered the oil through animal charcoal. Some expose the oil to sunlight in contact with animal charcoal for a week and do not filter the oil until then. But neither glass flasks nor even lead-lined boxes, nor, in fact, sun-bleaching, whether aided by animal charcoal, etc., or not, in any way coincide with the practical notions of the present day. Sun-bleaching of oils is only to be found in books, and is so long obsolete that any who attempted it on the large scale would nowadays be legitimately regarded as crazy. Undoubtedly, oil can be bleached almost water-white by the sun when either sunlight or daylight can get at it in every direction, but the interest on capital more than swallows up the profit, and the market for such an article is necessarily confined to artists, who often prepare their own oils.

Chevreul's Method of Bleaching Linseed Oil.—The following experiment by Chevreul is of great interest. Acting on the principle that linseed oil dries in consequence of atmospheric oxidation, Chevreul tried to find whether previous exposure to air conferred greater drying properties on linseed oil. He submitted linseed oil alone or mixed with turps to the action of air and light for 60 days. By comparison with untreated linseed oil he found that the drying capacity under these conditions was very great, as great in fact as manganese boiled oil, with the additional benefit that the oil was bleached; and as far back as 1851 he recommended the use of oil exposed to light for pale colours, and especially white zinc, which then gives its maximum of whiteness.

Refining Linseed Oil by Reducing Agents, Gaseous or in Solution—Refining by Hydrosulphites.—A process for refining linseed oil by hydrosulphites has been patented by A. Metz and Philip L. Clarkson. 200 gallons of raw oil are mixed with 600 gallons of cold water containing 200 lb. of hydrosulphite. The whole is agitated for 32 hours in a closed vessel, the oily layer is separated by decantation and the oil in the emulsion is recovered by petroleum ether.

Refining Linseed Oil by Lime.—Lime has been used to purify linseed oil, but Niegemann criticises its use for linseed oil owing to its forming soluble linoleates which darken the oil when heated. He prefers fuller's earth.

Bleaching Linseed Oil by Fuller's Earth.—Fuller's earth was, at one time, a purely English product, a sort of clay mined in different counties in the South of England. Within the last two decades it has been found in America, more especially Florida, and marketed under the high-sounding title of "Aluminium magnesium hydrosilicate". The Germans call it "Florida erde," but in Great Britain it still retains its name of fuller's earth, a name given to it centuries ago by the fullers of cloth owing to the facility with which it removes grease from fabrics. In bleaching linseed oil by fuller's earth, the process consists in agitating the oil with the required amount of fuller's earth, and then filtering the mixture. The agitation may be effected either by air or by a vertical shaft, fitted with horizontal arms or blades, or vice versa, a horizontal shaft fitted with vertical blades. To eliminate the colouring principle completely, it is necessary to secure the most intimate mixture of the oil and the fuller's earth. The linseed oil is run into the bleaching pan and fuller's earth added. The proportion of fuller's earth to oil varies greatly with the nature of the oil, its origin, and its depth of colour, and with the bleaching qualities of the oil, and to a very great extent, indeed, with the experience and skill of the bleacher. After the agitator has been put in motion, and a weighed quantity of fuller's earth added, samples of the oil at different stages of bleaching are taken from time to time and filtered into an 8 oz. bottle. More fuller's earth is added, until the oil has become sufficiently pale, when the mixture of oil and fuller's earth is filtered; the first runnings from the filter press return to the bleaching pan, until the oil comes away pale and clear. The proportion of fuller's earth runs from 2 to 5 per cent. of the weight of the oil. In the case of edible oils, as little fuller's earth as will be sufficient to bleach the oil should be used, as contact of the oil with the earth spoils the flavour, but this flavour may be neutralised by adding 1 to 2 per cent of soda-ash before filtration.

Filter Press Cake.—The residual cake left in the filter press consists of fuller's earth plus organic matter (mucilage, etc.), together with more or less oil, left in the cake. By steaming out the press the amount of this residual oil may be lowered to a minimum quantity. The oil, thus separated by steam, is disposed of according to its quality and amount. The residual oil still left in the sludge-cake, after steaming, if it eventually becomes considerable is not recovered as the expense would be too great. The press sludge is worthless.

Bleaching of Linseed Oil and of Drying Oils with Fuller's Earth—Removal of Mucilage.—Crude raw linseed oil is passed through a thick layer of fuller's earth or the earth mixed with the oil and passed through a filter press. It does not seem quite certain that all mucilage is removed from the oil by this treatment.

Elimination of Water.—Water is removed from linseed oil by treatment with fuller's earth in the cold. Weger collected the mucilage from a large quantity of oil, and tried to free the oil-charged mucilage from oil, by drying it on porous earthenware plates, but the attempt was not quite a success; it formed a yellow, gelatinous, transparent mass, which still dried very well on glass plates, in 3½ to 4½ days, with an oxygen absorption of 12·8 to 14. The removal of mucilage Weger contends is not so important, but linseed oil is seldom used for varnish-making without being treated with sulphuric acid or fuller's earth or calcined magnesia.

Behaviour of Bleached Crude Raw Oil on Oxidation.—Meister found that the oxygen absorption of a linseed oil rose from 19·5 per cent. for the untreated raw oil, to 20·7 for the oil bleached with fuller's earth.

Treating Wood Oil by Fuller's Earth.—A good stand oil, from wood oil, is obtained by heating the wood oil from 3 to 4 hours and bleaching the oil obtained with 5 to 10 per cent. of fuller's earth.

Removing the Green Coloration of Hemp-seed Oil by Fuller's Earth—Bleaching Perilla Oil Water-white.—The green colour of hemp-seed oil is removed by fuller's earth, and Perilla oil is bleached water-white.

Fuller's Earth, its Value for Oil Bleaching Purposes.—Neither the organoleptic properties of fuller's earth, nor its chemical analysis, fix its value for oil bleaching. A practical test can alone do so. When dry, fuller's earth sticks to the tongue, but other clays do so too. Unlike clay, it is not plastic; its combined water content is high. Its alumina content seldom exceeds 15 per cent. Its colour varies, naturally, from brown and grey to dark blue. Its distinguishing properties are fine grain, non-plasticity, and when broken up and thrown into water it forms a more or less flocculent mass. Its value depends on its absorbing and decolorising power. The mineral, after quarrying, is spread in thin layers on drying floors, or it is heated by fires in cylindrical driers. It is well ground before going through the driers. In drying it becomes white, and parts with upwards of 60 per cent. of moisture. When dry it is sifted into various degrees of fineness (100 to 120 mesh) and then bagged up for despatch.

Testing Fuller's Earth.—Fuller's earth is employed in America for clarifying and bleaching edible oils, and, as the earth from different localities varies very considerably in its efficiency, a ready method of testing its value is of great importance. T. G. Richert in "The Journal of Industrial and Engineering Chemistry" describes a series of tests which were applied for this purpose to four varieties of fuller's earth. (1) Locality unknown; (2) American; (3) English; (4) German. A good fuller's earth should remove all suspended matter, as much colouring matter as possible, and absorb a minimum of oil, at the same time the earthy taste which is imparted to the oil should be easily removable by deodorisation. The tests chosen were those of decolorisation and the amount of oil absorbed, the price of the earth being also taken into account. It is to be observed, however, that absolute values for the results of the tests cannot be fixed, the earths must be compared one with another with the same sample of oil, and the conditions of the experiments must be identical. In the bleaching tests eight experiments in each case were tried, with quantities of fuller's earth varying from 1 to 8 per cent., the colours of the bleached oil being determined by means of the tintometer. The German sample gave the best result with 3 per cent. of fuller's earth, an equally good result being obtained with 4 per cent. of the English sample. The amount of oil absorbed by a given weight of the earth was determined, and from this it was possible to calculate the presumptive loss, which amounted to (1) 8·3; (2) 40·8; (3) 8·0; and (4) 19·0 per cent. The cost of bleaching 100 lb. of the raw oil can therefore be shown by an equation, which the author gives in a simplified form as:—

$$V = \frac{x\,(100P + AO)}{100} \text{ cents.}$$

A being the presumptive loss, P and O the price in dollars for 100 lb. of earth and oil respectively, and X the percentage of earth required. It is satisfactory to note that the cost of bleaching with the English earth was the lowest, that is, 4·01 cents, the German being 5·24 cents, and the American 15·50 cents.

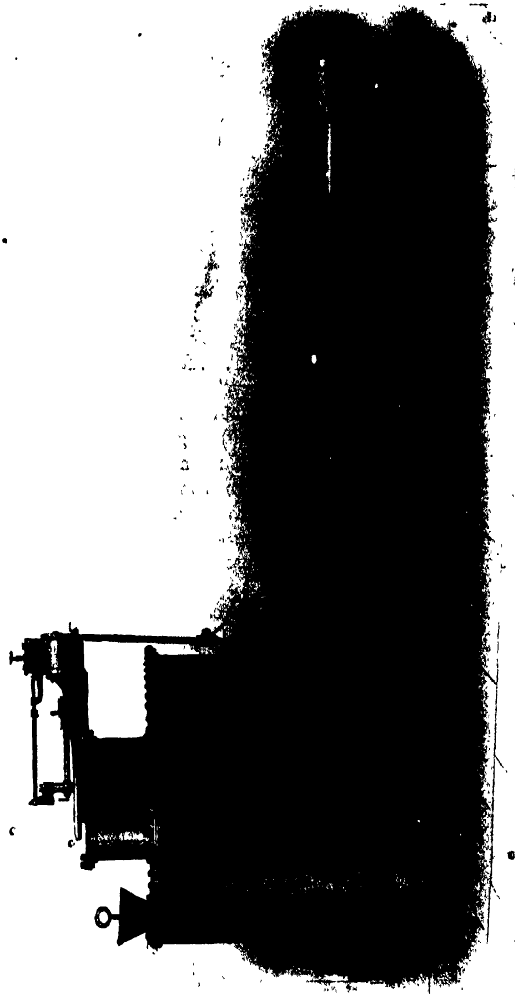


FIG. 38.—Filter press.

The steam-jacketed pans in use at the present day for refining linseed oil by aid of fuller's earth consist of cylindrical steel vessels with contracted neck at the top. The bottoms are made double so as to provide a steam jacket for heating, and the pan is also fitted with patent Vortex disc agitating gear which effects a very powerful rapid and intimate commingling of the fuller's earth with the oil. The pan is filled to the lower part of the neck with the oil to be treated previously heated to a temperature of 150° to 180° F. The right temperature is important. The Vortex mixer is kept in motion whilst the temperature of the oil is being adjusted, and as soon as it arrives at 150° F. the fuller's earth is added, great care being taken that the right proportion is used. It should be ground to a very fine powder and be perfectly dry and free from moisture—a most important point. Three to five per cent. is the amount generally used, but the quantity depends on the depth of colour of the oil, i.e. on the amount of colour to be removed. This the oil refiner can test by experiment by heating a small quantity and filtering it through filter paper in a tinned heated copper funnel before starting. As the oil deteriorates in taste and flavour by too prolonged contact with the fuller's earth it is very important to remove the latter as soon as possible. Hence to keep up a constant supply of oil to keep the filter at work it is better to work the pans on the twin system; whilst one pan is feeding the oil filters the other is being prepared and treated with fuller's earth. When the right proportion of fuller's earth is thoroughly commingled with the oil, the whole of the contents of the bleaching and mixing pan are pumped by a steam engine into the filter press. Pans of too great capacity are objectionable as the fuller's earth remains too long

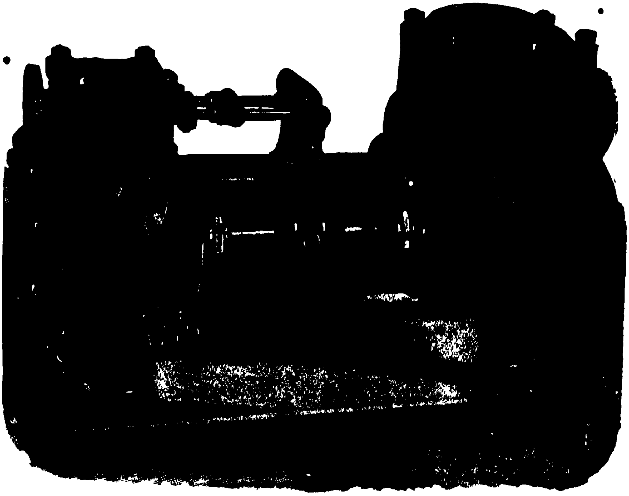


FIG. 39.—Steam pump for working in connection with hydraulic filters.

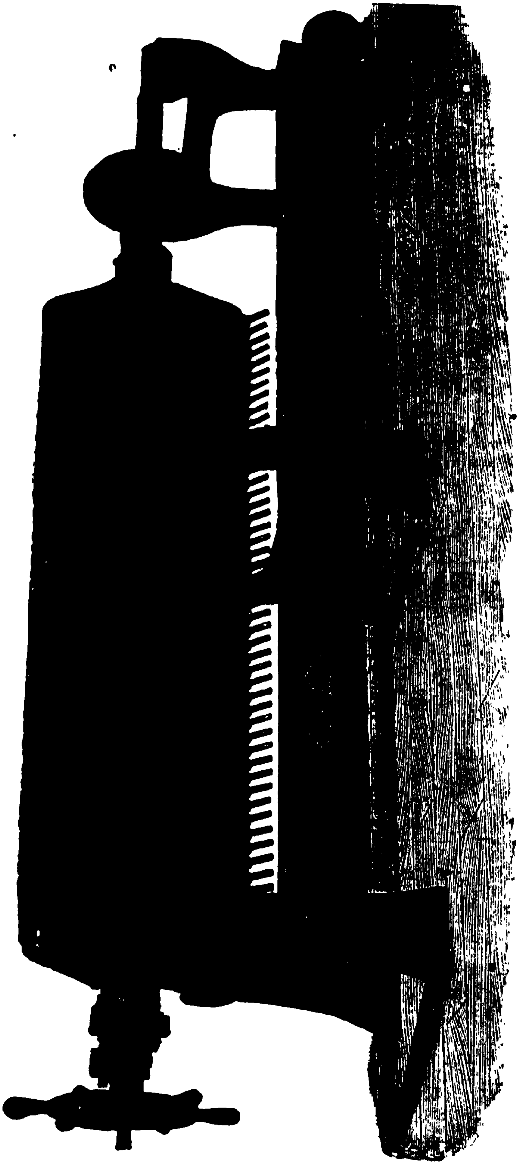


FIG. 40.—Special oil filter press, with 50 filtering chambers.

in mixture with the oil and imparts an earthy taste by the time the filter is filled with cake. The filter is so proportioned to the work to be done as to have a cake formed that will not be quite hollow. Steam is admitted into the centre feed channel of the press and finds its way into each of the hollow cakes. All the cocks are shut off except the six farthest away from the head. The steam passes through the centre of the press and first steams out the six cakes next the follower. When the steam has blown through these cakes so as to free them thoroughly from oil, the outlet cocks are shut off and the next six opened, and so on until all are steamed. When the press is opened to remove the fuller's earth it falls out in powder on the floor, little or no oil being left in it. Hence the steam should be dry steam; when viscid oils are being filtered such as linseed oil or castor oil, the filtration room should be warmed so that the whole mass of metal in the filter may be heated to the temperature at which it works best. With linseed oil this should not be below 90° F. With castor oil it should be still higher. Filters are also made with each of the plates steam-jacketed so that the contents of the oil filter may be maintained at any temperature required. These are used for treating solid fats, wax, paraffin, and vaseline.

A fuller's earth refining plant comprises one patent steam-jacketed Vortex mixing pan with self-contained engine, centrifugal mixing vane, trunk or circulating pipe, scroll deflecting plates, pipe work connecting engine exhaust to heating jacket, provided with thermometer, sampling cock, and charging hopper. One patent new model fuller's earth refining filter press, pyramid type, having arrangements for steaming out the cakes, provided with outlet cocks on each of the chambers and outlet shoot. Fitted with steam pump mounted on the head of the machine. The pipe work valves and fittings between mixing pan and feed pump on head of filter. One set of hydraulic chain and one set of chain filter cloths.

Refining Linseed Oil by Wood Charcoal.—Weger removed mucilage from linseed oil by treating the oil with wood charcoal.

Methods of Storing Raw Linseed Oil.—Galvanised iron reservoirs are to be preferred for storing linseed oil. Their base should be very wide in proportion to their height; they are generally covered by a badly-fitting lid, so that the air may be constantly renewed on the surface of the oil, but it is preferable to use a tight-fitting lid so as to exclude dust. In this case a current of air is set up by two tubes placed on opposite sides of the reservoir, thus starting oxidation, and thereby increasing the drying properties of the oil. It is also of importance to maintain the oil at a constant temperature, about 15° to 20° C.

Raw Linseed Oil Foots.—It is advisable to draw off the "foots" two or three times a year. It is an undeniable fact that oil kept for a certain time gives a better coating on drying, to that yielded by an oil fresh from the press. Speaking generally, linseed oil should not be used until after it has been "aged" for a year or two. Such oil is known as old tanked oil, and gives better results in varnish-making than can be obtained by any mere rapid process of bleaching freshly pressed mucilaginous raw oil.

When a varnish-maker buys clear and bright "old tanked" pure raw linseed oil, which, owing to prolonged storage, neither "breaks" nor "spawns" on heating, and so buys according to sample, which responds to the test for old tanked pure raw linseed oil, he is entitled to claim that the bulk delivered shall correspond with such sample in every way. For "breaking" or "spawning" is characteristic of recently crushed raw linseed oil, abounding in dissolved mucilage.

CHAPTER V.

CHEMICAL REACTIONS OF LINSEED OIL.

The Spectroscopic Examination of Linseed Oil.—Muller found that many oils show chlorophyll absorption bands when examined under the spectroscope. Animal oils do not do so. These absorption bands can therefore be utilised to detect a vegetable oil in an animal oil when the vegetable oil gives the spectrum of chlorophyll which, as Müller points out, occurs with linseed oil and also with olive oil. There are, in fact, three absorption bands; one very deep in the red, a feeble one in the orange, and a stronger one in the green. Sesame oil shows only a feeble band in the red, and castor oil shows no band at all. Donmer classifies oils according to their behaviour under the spectroscope when observed under a thickness of 12 millimetres:—

Oils exhibiting the spectrum of chlorophyll	Hemp-seed. Olive. Walnut (spectrum slightly visible but very decided blue and violet bands).
Oils exhibiting no spectrum . . .	Almond oil (sweet and bitter). Castor oil.
Oils absorbing all chemical radiations, the spectrum, instead of extending to the blue, the indigo, and the violet, stops short suddenly at full green . .	Colza-seed. Linseed. Mustard-seed. Rape-seed.
Oils exhibiting three bands in the chemical part, absence of green, orange, red bands characteristic of chlorophyll . .	Earth-nut. Colza-seed. Cotton-seed. Poppy-seed. Sesame.

Action of Halogens on Linseed Oil: Action of Chlorine and Bromine on Linseed Oil.—Lefort passed chlorine and bromine vapour into flasks containing layers of water and linseed oil, and found hydrochloric and hydrobromic in the state of solid compounds. Mulder led chlorine gas into water-free, but unheated, linseed oil and found that much hydrochloric acid remained in combination. The linseed oil was at first dark coloured (the dark coloration test given by chlorine with fish oil is valueless), then it became pale and at the same time solid. This solid body is scarcely soluble in water, readily soluble in ether and in potash lye. Mulder believed that a portion of the glycerine was split off by the chlorine. But the first action of chlorine on oils is to form addition compounds, and in the second place substitution compounds. Moreover, in the addition process, as it usually takes place, it stops short before the end of the reaction, although under suitable circumstances all the double bonds are satisfied by iodine chloride, and on that fact is based the well-known method of determining the iodine number.

Chlorine is used as a test for the presence of fish oil in linseed oil; this is supposed to darken in the presence of fish oil, but pure linseed oil darkens too, so the test is indecisive if not unreliable (see under fish oil as an adulterant of linseed oil, p. 174).

Action of Sulphurous Acid on Linseed Oil.—By treating linseed oil with sulphurous acid, Sacc caused the separation of white flakes, which he described as gypsum (!) Mulder investigated the point by first treating linseed oil with sulphurous acid and then burning it. He found about 0·03 per cent. of ash and contradicted Sacc's assertion that linseed oil usually contains a large amount of lime. Moreover, Mulder, by treating linseed oil with sulphurous acid, obtained a white precipitate, insoluble in water, soluble in alcohol and ether. Further, Mulder found sulphurous acid to exert a reducing action on linseed oil which then appears to contain much sulphuric acid.

Action of Ammonia on Linseed Oil.—Rowney treated drying and non-drying oils with alcoholic ammonia with frequent shaking for a long time. With linseed oil he obtained a highly coloured resinous substance, and a little of a white solid crystalline body. With olive oil the behaviour was different. Rowney and Mulder described the white body as an amide, behaving like a soap. The red resinous substance Mulder identified as red linoxic acid. It has since been found that the linoleic acid of linseed oil contains higher unsaturated fatty acids than oleic.

Heat of Combustion of Linseed Oil.—The heat of combustion increases, generally, with the molecular weight and differs in that respect but little as regards fats and oils. Sherman and Snell found the heat of combustion of fresh linseed oil at constant volume to be 9364, at constant pressure, 9379 calories. It lowers on oxidation.

Action of Sulphuric Acid on Linseed Oil.—Chevreul pointed out that oils and fats when treated with concentrated sulphuric acid liberated glycerine. Sacc treated linseed oil with concentrated H_2SO_4. Sulphurous and formic acids were disengaged. The linseed oil was coloured purple red, then violet, then black. The product washed with water was amorphous and appeared in the form of long strings. It was soluble in alcohol; with alkalies it gave a yellow resinous soap. Mulder did not use H_2SO_4 in excess, it gave off no gas, and the reaction product in water eventually became colourless.

It was more readily saponifiable than linseed oil itself. Mulder believed that there was only free oleic acid and no free linoleic acid which was held fast locked up by the glycerine. An accurate examination of the reaction between linseed oil and sulphuric acid has not yet been made, but the heat of the reaction forms a valuable test, being far greater with linseed oil than with any other oil. Maumené was the first to utilise the different temperatures to differentiate between different oils, and Jean produced his thermacolemater for use in applying the test. Lately Tortelli has brought out an improved apparatus. The test is readily applied, but its application requires care. The Maumené number or thermo number of linseed oil varies between 90° C. and 145° C. Moreover, the Maumené number gives parallel results with the iodine absorption results.

Action of Nitrous Acid HNO_2 *on Linseed Oil.*—In the year 1819 Poutet treated oils with nitrous acid and claimed as the result of the reaction to be able to differentiate between drying and non-drying oils, as the former remained fluid whilst the latter solidified in a longer or shorter time. The basis of this solidification is the conversion of the oleic acid of m.p. 14° C. (57·2° F) into its isomer elaidic acid. It is said by some to be unreliable. But that statement comes from those who have never applied the test in actual practice in the buying and selling of olive oil. Lidoff treated linseed oil with nitrous acid HNO_2 and found it to remain fluid but completely changed. Its specific gravity rose from 0·932 to 0·971, and the oil after washing contained combined nitrogen. Possibly the nitrous acid fixed itself directly on the double bond.

Action of Nitric Acid on Linseed Oil.—Linseed oil treated with nitric acid behaves differently to oleic acid (Bromeis). The product is a tacky, deep red mass containing pimelic acid, $C_7H_{12}O_4$, suberic acid, $C_8H_{14}O_4$, oxalic acid, $C_2H_2O_4$, and an acid which Bromeis afterwards termed margaric acid. Sacc confirmed the above results. Mulder did not repeat the experiment. He termed the red product linoxic acid. However, he treated linseed oil, at the ordinary temperature with a small quantity of strong nitric acid, but was unable to confirm Jonas' statement that the oil, so treated, dried more rapidly. According to Livache, thick boiled linseed oil, treated with dilute nitric acid, gives a brown elastic substance, which no longer sticks to the fingers. A. Lidoff passed nitric-anhydride into an ethereal solution of linseed oil. He found simultaneous nitration and oxidation, and a thick yellow oil was formed, insoluble in water, and combustible without explosion, which absorbs no more iodine. In ethereal solution it is reduced by stannous chloride, H_2S, or aluminum amalgam to a product varying from syrupy to a solid mass, which is no longer soluble and which Lidoff regarded as lying between fat and albumen.

Heat of Bromination of Linseed Oil.—Chloroform gives a slightly higher rise than carbon tetrachloride, as would be expected; this was found to be 1·7° with the apparatus here described. Archbutt and Jenkins find that the presence of water, either in the bromine or the oil, is apparently of no influence.

The results obtained vary with each calorimeter; hence, to make them comparable, they must, as in the Maumené test, be referred to some standard. Such a standard has been found in sublimed camphor, which can be prepared in sufficient purity; $7\frac{5}{10}$ grammes are dissolved in carbon tetrachloride and brominated, giving an average rise of 4·2°. The rises in temperature obtained with the various oils were divided by this number, giving a specific temperature reaction; if this be multiplied by a factor—found by dividing several of the iodine numbers by this specific temperature—the iodine value of any sample may be quite closely determined; this is shown in the following table, the factor being 17·18:—

TABLE SHOWING THE RELATION OF THE BROMINATION AND IODINE VALUES.

Name of Oil.	Specific Temperature Reaction.	Iodine.	
		Calculated.	Found.
Neatsfoot	3·286	56 5	59·1
Tallow	3·348	57·4	57·2
Prime lard	3·715	63·8	63 8
Sperm	4·191	72·1	73·2
No. 1 lard	4·096	70·3	73·9
Olive	4·762	81·8	82 0
Cotton-seed	5·667	97·3	103·0
Corn	6·381	109·5	107·8
Cod	8·002	137·4	135·0
Linseed	9·049	155·6	160·0
25° paraffin	1·643	28·2	10·1
300° lantern	1·190	20·5	0·0

In the case of the hydrocarbon oils the discrepancy may be due to the fact that there is substitution by the bromine and none with the iodine.

Catalytic Action of Metallic Magnesium on Linseed Oil in Presence of Hydrogen.—Meusel & Co., D.R.P. 201,906, heat linseed oil at the ordinary pressure, or in vacuo, for 3½ to 4 hours with 0·5 to 1·0 per cent. of powdered magnesium with the formation under the action of hydrogen gas of a solid, readily moulded, fusible product. The thickening occurs without the formation of a magnesium soap.

Action of Hydrogen Aided by Catalyst on Linseed Oil.—When hydrogen is passed into linseed oil at a high temperature no reaction ensues. Hydrogen atoms are fixed on the double bonds, but aided by a catalyst it succeeds much better.

As Dr. Holde states, oleic acid, the most important constituent of all semi-drying liquid oils, requires only 2 parts of hydrogen to 282 parts of oil in order to get stearic acid, while linoleic and linolenic acid require 4 and 6 parts respectively, to 280 and 278 parts. Ricinolic acid, which contains 1 atom of oxygen more than oleic acid, forms an oxystearic acid which has a very high melting-point, but which also contains only 2 atoms more of hydrogen than the original acid.

Saul and Roth rubbed up 4 grammes linseed oil with 2 grammes gum-arabic, using colloidal palladium as catalyst. When the mass thickened it was heated to 50 to 70° C. and hydrogen passed through it. The first hydrogenisation left a white hard mass of m.p. 56 to 63° C. with the iodine number of 5·6. The product was white and pulverisable, readily soluble in $CHCl_3$ and CS_2 and melted at 61 to 65° C. Bedford did not reduce linseed oil itself, but operated with linoleic acid using finely divided Ni as catalyst.

There are, besides ferments and enzymes, other agents used for the splitting of linseed oil. The first of these agents is water at a temperature of 200° or under a pressure of 15 atmospheres. Taking the fatty acids of linseed oil as ROH, the action of saponification may be represented thus:—

$$C_3H_5(OR)_3 + 3H_2O = C_3H_5(OH)_3 + 3ROH.$$

It is disputed whether this reaction occurs in one stage, so as to yield free fatty acid and glycerine, or whether there are intermediate products formed, viz. di- and monoglycerides thus:—

$$\text{(A)}\ C_3H_5(OR)_3 + H_2O = C_3H_5(OH)(OR)_2 + ROH$$
$$\text{(B)}\ C_3H_5(OH)(OR)_2 + H_2O = C_3H_5(OH)_2(OR) + ROH$$
$$\text{(C)}\ C_3H_5(OH)_2(OR) + H_2O = C_3H_5(OH)_3 + ROH.$$

To test the point R. Fanto completely saponified linseed oil with aqueous potash, but could not detect either di- or monoglycerides in the products of the reaction. Later on I. Kellner asserts that linseed oil is saponified in different stages, but on saponification with aqueous lyes the three phases of the reaction follow each other so quickly that it is impossible to follow them.

Alcoholysis.—During saponification by aqueous alkali the reaction is impeded by the fact that the fat is insoluble in water and therefore the act of saponification is prolonged. Saponification by alcoholic potash is much more rapid. As the oil is to a certain extent soluble in alcohol the decomposition is so far facilitated that the glycerine ester is converted into an ethyl ester, and the first stage of the splitting up then becomes:—

$$\text{(A)}\ C_3H_5(OR)_3 + 3C_2H_5OH = C_3H_5(OH)_3 + 3C_2H_5(OR)$$
$$\text{(B)}\ C_2H_5OR + H_2O = C_2H_5OH + ROH.$$

The term alcoholysis is applied to the above reaction in contradistinction to "hydrolysis". In the former case it follows that when the amount of alkali is not sufficient to convert all the fatty acids into soap the whole of the glycerine is separated—

$$C_3H_5(OR)_3 + KOH + 2C_2H_5OH = C_3H_5(OH)_3 + ROK + 2C_2H_5OR.$$

When alcohol, therefore, is used as the solvent and the glycerine dissolves as an ethyl ester, the change expressed by the above reaction takes place very rapidly in the cold—cold saponification. Henriques dissolved 50 grammes of linseed oil in 50 c.c. petroleum ether, added 25·75 c.c. normal alcoholic potash (for complete saponification 9·610 grammes would have been necessary), agitated until completely mixed, and let stand 6 hours. The liquid gave no further coloration with phenolphthaline, and the glycerine was separated quantitatively, the ethyl ester distilled above 360° C., and was thus separated from the non-volatile glycerine ester. It was found later on by A. Haller that for the separation of glycerine as ethyl ester no alkali is required, and that the same reaction occurs more readily with alcoholic hydrochloric acid. By treating linseed oil with excess of methylic alcoholic hydrochloric acid for 6 hours, in a reflux condenser, the whole of the glyceride was converted into a methyl ester. During hydrolysis and alcoholysis both alkali and acid act catalytically. When linseed oil is saponified by soda lye, or by alcoholic soda, by dilution of the alcoholic solution of the soap in water, there is obtained, in the aqueous solution, (1) all the glycerine, (2) all the fatty acids of the linseed oil as soda soap, and (3) the excess of caustic soda. The soda soap may be separated out from this solution by "salting out". Ten per cent. of common salt is dissolved in water, by the aid of heat, and added to the solution, with constant stirring. Glycerine, caustic soda, and sodium chloride remain in solution. The soda soap separates out, almost quantitatively, on the surface. It is filtered off, and washed with a 10 per cent. solution of common salt. Hard soap is made by the salting-out process, but linseed oil is only used in making soft soap. By saponifying linseed oil by caustic potash and dissolving 10 per cent. of common salt in the aqueous solution, the fatty acids are separated, as soaps, and an equivalent quantity of potassium chloride passes into solution

CHAPTER VI.

LINSEED OIL FATTY ACIDS.

Splitting up of Oils and Fats.—When a solution of neutral soap is dissolved in water the solution does not react neutral, but alkaline. This is due to the high molecular weight and the weakly acid character of the fatty acids. Their soaps are dissociated by water, so that the solution contains at one time free alkali and at another time acid soap. Excess of alkali stops this dissociation, also alcohol. Kanitz has shown that, in a mixture of 40 per cent. alcohol and 60 per cent. water, dissociation does not occur. The splitting up of fats constitutes a great industry in which fatty acids are prepared for candle or soap manufacture. Fatty acids are marketable products. These do not include linoleic acid, which is, however, extensively used in the manufacture of driers. In the preparation of fatty acids for the candle trade, autoclaves are used, the decomposition by water of the fat occurring at a pressure of about 8 atmospheres, with the addition generally of quicklime, magnesia, or zinc-dust. There are also Twitchell's method, and the fermentative splitting up of fats. In Twitchell's method the splitting up is effected by steam at the ordinary temperature, using naphthalen stearo-sulphonate as catalyst. In the fermentative splitting up of fats, lipase, a ferment which occurs abundantly in castor oil seed, is used as the hydrolysing agent. A similar ferment has been found in linseed and in linseed oil cake. This method is little used, the zymogen cannot be obtained as an active enzyme. Linseed, however, contains an active lipase, different from that of any other seed. None of the splitting processes in use give quantitative results, and technical linoleic acid contains 5 to 10 per cent. of neutral undecomposed oil.

The Intimate Chemical Composition of Linseed Oil.—Like all other oils and fats, linseed oil consists of the elements carbon, hydrogen, and oxygen. It does not contain sulphur, except it be in traces, and then only when the linseed is highly impure, from cruciferous seeds, is the sulphur content of linseed oil appreciable. Extracted oil contains nitrogeneous substances in small quantities. The above three elements group themselves together in linseed oil, (1) as glycerine, (2) as fatty acids, both being present as glycerine esters. The splitting up of these esters is best done in the laboratory, by heating with excess of alcoholic potash (or soda) lye. On diluting the alcohol a mixture of (1) glycerine, (2) potash soap, and (3) free alkali is obtained. If this solution be boiled with excess of hydrochloric or sulphuric acid, the soap is decomposed, the fatty acids, insoluble in water, separate as an oily layer on the surface, and can be separated by a separating funnel from the aqueous acid liquid. That in the latter there remain no fluid fatty acids, Mulder has shown by a distillation experiment. It contains all the glycerine, which, however, is not pure. By evaporation with carbonate of potash lye, and extraction of the residue with acetone, the glycerine may be isolated.

The Mixed Fatty Acids of Linseed Oil.—That the mixed fatty acids of linseed oil are to a large extent fluid, and that only a small amount of solid fatty acids is present is shown by their behaviour on cooling. They partially crystallise at 15° C. (59° F.) and liquefy on warming to 20° C. (68° F.). The solid fatty acids have a higher melting-point when freed from the liquid fatty acids. When the mixed fatty acids are cooled to 0° C. (32° F.), the solid fatty acids do not separate out quantitatively, therefore, the portion that has crystallised out, as a general rule, contains much fluid fatty acids. The separation is best carried out by cooling of alcoholic solution of the fatty acids, a method first adopted by Chevreul, and later on by Mulder. Mulder has shown, in regard to Warrentrapp's method, which rests on the principle that the lead salts of the fluid fatty acids are soluble in ether whilst the solid fatty acids are insoluble, that this method is not trustworthy, as the lead salts of the solid fatty acids are not completely insoluble in ether, and that the separated lead salts of the solid fatty acids are still coloured yellow, and, therefore, impure. Moreover, the fluid fatty acids still contain insoluble lead salts.

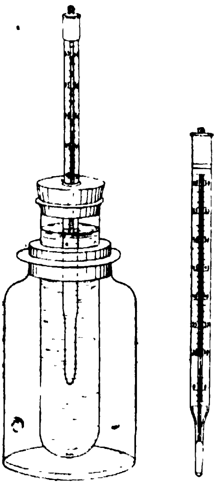


FIG. 41.—Wolffbauer's method of determining the solidification-point of the mixed fatty acids of different drying oils.

Melting-Point of Fatty Acids.

The Iodine Number of the Liquid Fatty Acids of Linseed Oil (*the Inner Iodine Number*).—The saturated solid fatty acids absorb no iodine, so if the iodine absorption of the fluid fatty acids, the inner iodine number, be known, so also is that of the mixed fatty acids and of the oil itself known. The solid and fluid fatty acids are separated by Warrentrapp's method thus: 10 grammes of oil are run into a 300 c.c. Erlenmeyer flask and heated with 40 c.c. in alcoholic potash, until complete saponification is effected. Phenolphthalein is added, and the soap neutralised with strong acetic acid. Enough water is added to equal that of the alcohol, then a solution of 10 grammes of lead acetate in 100 c.c. 50 per cent alcohol. The whole is heated on the water-bath until the lead soap is solid, the flask with stirring rod is removed, and the whole allowed to stand overnight. The fluid portion is run off through a filter, and the small amount of lead soap added later on to the main portion. The lead soap remaining in the flask is drenched with alcohol and the flask and contents put to dry in a warm place. To the dried lead soap 100 c.c. ether is added, and shaken until the larger lumps have completely broken up and the insoluble lead soap floats in the solution, in the form of a flaky precipitate. The whole is allowed to settle and the ethereal solution filtered into a separating funnel. The washing of the precipitate is unnecessary when only the inner iodine number is to be determined. The ethereal solution is agitated with hydrochloric acid, in excess, to decompose the lead salt. When the ethereal solution has completely clarified, the acid aqueous fluid and the lead chloride are separated from the ethereal solution of fatty acids in a second separating funnel; there it is shaken with aqueous lye, containing about 2 grammes NaOH or KOH. To cause the two layers to separate out sharply 10 to 20 c.c. of alcohol are added, and repeatedly shaken. The unsaturated fatty acids are dissolved in the alkaline solution from which they are recovered on acidulation by hydrochloric acid, and shaking with petroleum ether. The latter should not contain any fraction boiling above 60° C. and should be completely volatile on the water-bath. By the above method of purification the unsaturated fatty acids are separated from the unsaponifiable on the one hand, and the oxyacids on the other. The presence of lead starts catalytic auto-oxidation, so the formation of oxyacids cannot very well be completely prevented, but it can be very much reduced when the extraction of the lead soap and the distillation is conducted in a stream of hydrogen. Warrentrapp's method was soon found to be defective, as a non-negligible portion of unsaturated fatty acids remains in the residue from the ethereal solution of the lead salts, so that the separated lead salts still absorb iodine. Fahrion found 10·6 to 14·3, Lewkowitsch 22·3, and later on 19·2. It is important to observe that it is oleic acid which remains in the saturated fatty acids and so increases the inner iodine number. Conversely there remains a small quantity of solid fatty acids in the fluid portion, and, during auto-oxidation, takes the place of a portion of the linolenic acid. Both lower the inner iodine number, so that the latter is generally low. Fahrion found for the linseed oil used outer iodine number 280·9?, and for the inner iodine number 203·3, 204·6, and 205·2, although in shaking up with ether the lead was replaced by a baryta salt.

THE IODINE NUMBER OF (*a*) DIFFERENT SAMPLES OF LINSEED OIL AND (*b*) OF THE LIQUID FATTY ACIDS DERIVED THEREFROM.

	(*a*) "Outer Iodine Number."	(*b*) "Inner Iodine Number."
Cold pressed linseed oil	179·4	201·4
Italian linseed oil, 1898	173·4	190·1
" " " 1899	176·8	193·0
Indian " "	184·0	208·0

Numerous attempts to render Warrentrapp's useful method for the separation of fatty acids accurate, have been made. Farnsteiner replaces ether by benzol. On heating, the lead salts of the saturated fatty acids dissolve, but on cooling from 8 to 12° C. they are quantitatively separated, and only the unsaturated lead salts remain in solution Fahrion tried this method, but found no great advantage over the ordinary method. The insoluble lead salts were coloured yellow, and gave an iodine absorption of 13·9. Farnsteiner claims also to have discovered a method of separating oleic acid from the highly unsaturated fatty acids. He converts the mixed fatty acids into the baryta salt and treats this whilst warm with a mixture of 95 per cent. benzol and 5 per cent absolute alcohol. Barium oleate dissolves therein on cooling to about 0°; it is quantitatively separated whilst barium linoleate and linolenate remain insoluble, but this method is not accurate. A method of Partheil and Ferié, in which the lithium salt is used for separation, is quite unreliable.

Fahrion's Oxyacids. Their Estimation.—It has been repeatedly proven that (1) linseed oil and (2) linseed oil fatty acids absorb oxygen from the air. Amorphous oxyacids are thus formed from (*a*) linoleic and (*b*) linolenic acids, as first pointed out by Fahrion. They are characterised by their insolubility in petroleum ether; their glycerides are, however, soluble therein, so that a highly oxidised linseed oil still may remain soluble in petroleum ether. If the oil in question be saponified, the separated fatty acids are still soluble in ordinary ether, but partially insoluble in petroleum ether. The quantitative estimation of these acids is performed in the same way as the determination of the Hehner number. The oxyacids occur as light flakes, and are separated from the petroleum ether solution of the fatty acids by filtration. Or, if it be desired to handle them in large quantities, a separating funnel is used, so that the petroleum ether solution may be drawn off clear. The oxyacids are dissolved in warm alcohol, the solution cooled, and filtered into a platinum dish. The alcohol is evaporated on the water-bath, the residue dried, weighed, heated, and again weighed; the difference gives the oxyacids. Quite fresh linseed oil should naturally be free from oxyacids, but, in actual practice, traces are always found. Again, linseed does not come fresh to the press; it has a long sea-voyage behind it. Moreover, the practice of foreheating the seed induces slight auto-oxidation of the linseed oil.

No.	Age of Oil.	Iodine No.	Oxyacids Per Cent.
I.	Two months	170·46	0·65
II.	Three years	174·03	0·70
III.	Two months	177·25	0·88
IV.	Seven ,,	176·23	0·56
V.	—	170·05	0·73

But linseed oil fatty acids are much more readily oxidised than linseed oil itself, and it must not be forgotten that, during the process of analysis, small quantities of new fatty acids are formed. If linseed oil mixed fatty acids be heated for 2 hours in the water-bath in an open porcelain basin at 105 to 110° C., 10 per cent. becomes insoluble in petroleum ether. It therefore contains oxyacids, which Mulder wrote so much about, although petroleum ether was unknown to him.

Like Liebig, Schuler, who, like Mulder, occupied himself with linseed oil, speaks of the solid fatty acids as palmitic acid, but without any close examination. Mulder saponified linseed oil with aqueous potash lye, and precipitated the soap with lead acetate, kneaded the lead salt with warm water, and, whilst still moist, extracted it with ether. The insoluble lead soap, mixed with white lead and lead hydroxide, was decomposed by hydrochloric acid, and the fatty acid submitted to fractional crystallisation from alcohol. Mulder thus obtained (1) palmitic acid, $C_{16}H_{32}O_2$, of melting-point 62° C. and (2) myristic acid, $C_{14}H_{28}O_2$, of melting-point 53° C. Both were contaminated after repeated crystallisation by a red resinous substance, removed by animal charcoal. The mother liquor contained a buttery substance, which, on attempts to crystallise it, only left a reddish, completely saponifiable resin, readily soluble in alcohol. As to the composition of this resin, Mulder was quite right in regarding it as a linoleic-acid residue which remained in the lead soap, and, in the sequence of different operations, became, in course of time, oxidised. Mulder recognised lauric acid, but Hazura could find no trace of it. We know now that it is well-nigh impossible that a single individual of a mixture of three or more solid fatty acids should be completely pure and free from fluid fatty acid by mere separation by crystallisation. When it is confidently asserted on the authority of Mulder's experiments that the greater part of the solid fatty acids of linseed oil consist of palmitic acid and myristic acid, it must not be lost sight of that Mulder had only a very small quantity of these on his hands for examination purposes. Moreover, during the alcoholysis of linseed oil, with subsequent fractionation and saponification of the methyl ester, besides palmitic and myristic acids, Haller found an appreciable quantity of stearic acid, $C_{18}H_{36}O_2$, melting-point 69° C., and a small quantity of arachidic acid, $C_{20}H_{40}O_2$, melting-point 77° C.,

Solid Fatty Acids of Linseed Oil.—Liebig described the solid fatty acid that can be separated from the mixed fatty acids of linseed oil as palmitic acid. Unverdorben found that linseed oil contained stearic acid as well as palmitic acid. Bromeis isolated the solid fatty acids by treating the linseed oil with nitric acid, by which treatment they remain to a great extent unchanged and can be crystallised from alcohol. He termed them margaric acid; likewise Sacc, who obtained them in the same way and gave them the formula $C_{16}H_{32}O_2$. Sacc knew that the solid fatty acids obtained by Warrentrapp's method were impure. The ether-insoluble lead salts contained basic lead linoleate. He examined into the matter of the separation of the liquid and solid acids further, and in a very interesting way. He saponified linseed oil with caustic soda lye, and separated the soda soap from the solution by excess of common salt. The semi-dried soap was exposed in a thin layer in an airy place and kept warm, so that it rapidly absorbed oxygen, and dried with a yellow colour. After two or three weeks it was brought into solution by strong soda lye, which was coloured brown. The whole operation lasted two to three months and eventually gave an almost white soap. This was decomposed by hydrochloric acid and the fatty acid crystallised from alcohol, melting-point 60° C. (140° F.) C = 75·8, H = 12·5, O = 11·7 per cent. = 100; $C_{16}H_{32}O_2$ requires C = 75·0, H = 12·5, O = 12·5. It thus follows that Sacc was the first to show the purity of the auto-oxidation products of the liquid fatty acids of linseed oil.

Fluid Fatty Acids of Linseed Oil. Chevreul's, Gottlieb's, and Voelcker's and Laurent's Results.—Amongst the fluid fatty acids of linseed oil, Chevreul only described oleic acid, the correct composition of which, as $C_{18}H_{34}O_2$, was first determined by Gottlieb and Voelcker. Laurent must be credited with the discovery that linseed oil must contain other fluid fatty acids than oleic acid, as he found linoleic acid to behave quite differently under the elaïdin test, and under vacuum-distillation, from ordinary oleic acid. *Sacc's experiments.*—The next results as to the composition of linoleic acid were obtained by Sacc, who experimented on the subject afresh. He saponified cold-pressed linseed oil with lead oxide, extracted the lead soap by agitation with ether, decomposed the ethereal solution by sulphuretted hydrogen, and subjected the linoleic acid so obtained to combustion. To the data so obtained (C 76 per cent., H 10·7 per cent., O 13·2 per cent.) corresponds the formula $C_{23}H_{39}O_3$. *Mulder's criticism.* — Mulder justly pointed out that, from the above data, Sacc's linoleic acid had absorbed much oxygen. *Action of nitrous acid on linoleic acid and nitric.*—Sacc found that linoleic acid when treated with nitrous acid gave no elaïdin. Treated with nitric acid it first of all gave a reddish resin, afterwards found to be suberic acid, $C_{18}H_{14}O_4$.

Schuler's Method of Preparing Linoleic Acid.—Schuler saponified linseed oil with caustic soda, salted out the soap, precipitated the aqueous solution with calcium chloride, agitated the lime soap with ether, decomposed the ethereal solution with hydrochloric acid, and dried it, at a low temperature, in a stream of hydrogen. To purify it still further, the linoleic acid was converted into a baryta salt, the latter, crystallised from alcohol, agitated with ether, and the ethereal solution treated as above. Schuler describes the linoleic acid so obtained as a pale yellow, very limpid fluid with a weak acid reaction, and a pleasant taste at first, but unpleasant later on. The combustion results (C 75·9 to 76·2 per cent., H 10·9 to 11·4 per cent.) correspond to the formula $C_{16}H_{28}O_2$.

Mulder's Objections.—Mulder raised the objections to Schuler's linoleic acid that it had absorbed much oxygen and that it was impossible to talk of crystallisation of the baryta salt, as it separates from an alcohol solution in flakes. It is now evident that the numerous purifications were not effected without considerable loss of substance, so that the fatty acid separated, and analysed, had a different composition from the original. Schuler found too little metal in his linoleic salts, and therefore the true formula may be $C_{17}H_{30}O_2$. Mulder concluded from the above results, that Schuler's linoleic acid contained ordinary oleic acid. Schuler's formula was next attacked by O. Sussenguth who treated linoleic acid with bromine.

Sussenguth's Impure Hydrobrominate from Linolenic Acid.—Hydrobromic acid was evolved with great evolution of heat. He agitated the product with ether, crystallised the insoluble from alcohol, and so obtained crystalline plates, a fatty acid with the formula $C_{16}H_{26}Br_4O_4$. He had in reality obtained impure hexabromlinolenic acid. Mulder experimented on the oxidation of linoleic acid and its salts. He examined the behaviour of linoleic acid, under repeated oxidation, as a result of which the more often pure linoleic acid is treated, the less there remains of it, and the more impure is the oxidation, and again, free linoleic as well as its salts is readily oxidised and useless for analysis. It follows therefore that free linoleic acid cannot be used for general analysis, and great difficulty is experienced in preparing pure salts from it and in correlating the carbon, and hydrogen, and metal, with the correct formula for linolic acid. The metal content is very contradictory, the salt containing too little. Mulder tried to find whether it was entirely due to hydrolysis or to the formation of basic salts, that whilst approaching the right weight they were no longer soluble in ether. A neutral salt was necessary for solution in ether, said Mulder, who further stated that a satisfactory metallic salt cannot be prepared from linoleic acid.

Fahrion's Method of Preparing Pure Metallic Linoleates.—According to Fahrion, the preparation of pure metallic linoleates is not so difficult. He saponifies the linseed oil with caustic soda, nearly neutralises the aqueous solution with acetic acid, precipitates with barium chloride, extracts the baryta salt with ether, and evaporates the ethereal solution, without further treatment, in a platinum basin on the water-bath. The residue contains 20·2 per cent. baryta (barium linolenate = 19·9 per cent.).

In spite of all the above drawbacks Mulder believed from the C and H content of a lime and a copper salt that he had confirmed Schuler's formula. However, the above figures in no wise correspond with $C_{16}H_{28}O_2$, but according to the theory of that time, which regarded these salts as addition products of metallic oxide and acid anhydride, the anhydride of $C_{16}H_{28}O_2$ $(3C_{32}H_{54}O_2 + 2C_{16}H_{28}O_2)$; when more closely inspected Mulder's salts had absorbed much oxygen. At the same time they are less prone to oxidation than Mulder thought.

Hazura's Method of Saponifying Linseed Oil.—Hazura saponified linseed oil with alcoholic potash, dissolved the soap in much water, neutralised with acetic acid, precipitated with lead acetate, extracted the still moist precipitate with ether, decomposed the ethereal solution, by acid, and dried the residue, over H_2SO_4. Combustion gave C = 77·48 and 77·35 per cent.; H = 10·85 and 10·79 per cent., calculated for linolenic acid; C = 77·7; H 10·8.

Mulder's Belief in the Presence of Oleic Acid in Linoleic Acid.—Mulder only accepted Schuler's linoleic acid formula of $C_{16}H_{28}O_2$ with reservations. He asserted that no one can deny that pure linoleic acid has not yet been prepared, to which the formula $C_{16}H_{28}O_2$ can be applied. This doubt was intensified by Mulder's firm belief that linoleic acid also contained oleic acid, $C_{18}H_{34}O_2$, or at least some other similar acid. As he could not fractionally crystallise the salts of linoleic acid he attempted to prepare them in another way. He agitated completely dry linseed oil with ether, which left behind a thick fluid quite colourless body, soluble in ammonia and soda lye. When this substance was converted into a lead salt and the latter shaken with ether, and the ether soluble salt decomposed, a fluid fatty acid was obtained.

Mulder's Dried Film of Lead Linoleate.—Finally Mulder left an ethereal solution of lead linoleate to evaporate in the air. The lead salt, so obtained, gave on decomposition an oily acid, which did not dry and therefore was not linoleic acid. As the thick fluid gave no elaïdic acid, with nitrous acid, Mulder regarded it as oxidised oleic acid. Mulder describes linoleic acid as a colourless oil which rapidly becomes coloured in the air, which can be cooled below 0° C. without solidifying. The K, Na, NH_3 salts are soluble in water and alcohol, the Ba and Ca salts in hot alcohol, the Ca, Ba, Cu, Pb salts in ether. On fusion with caustic alkali linoleic acid gives hydrocarbides and a volatile acid. Hydrogen and acetic acid were not found.

Hazura's Linoleic Acid.—But Hazura obtained both the latter, by fusion of the oleic acid, from hemp-seed oil with potash. He prepared this linoleic acid by Schuler's method with the qualification that the baryta salt was only dissolved in alcohol. The combustion gave figures which corresponded with the formula $C_{18}H_{32}O_2$.

The C_{18} Nucleus of Peters.—That linoleic acid contained the nucleus C_{18} Peters showed thus: he heated it with hydriodic acid and red phosphorus for 8 to 10 hours at 200 to 210° C. and treated the product with sodium amalgam and thus obtained stearic acid, $C_{18}H_{36}O_2$, melting-point 69° C.

Duff and Reformatsky's Researches.—Duff and Reformatsky prepared Schuler's linoleic acid in a pure state but from ethyl linoleate. It was converted by hydriodic acid into moniodo-stearic acid, $C_{18}H_{35}O_2$, and the latter reduced by zinc and hydrochloric acid to stearic acid, $C_{18}H_{36}O_2$. The yield of the latter was, of course, only small. Whilst the inaccuracy of Schuler's formula was acknowledged, the above authors, in contradiction of Mulder, still regarded linoleic acid as a simple substance. K. Hazura was the first to obtain oleic acid from Mulder's supposed linoleic acid, and later on to show that, besides oleic acid, $C_{18}H_{34}O_2$, another acid, $C_{18}H_{32}O_2$, but in much larger quantity, a still stronger unsaturated fatty acid, $C_{18}H_{30}O_2$. Hazura used an oxidation method by which the unsaturated fatty acids were dissolved, in excess of caustic potash, and the solution decomposed by permanganate. This method was first used by Kehule in the oxidation of fumaric and malic acids, whilst Sayteff was the first to use it for fatty acids of high molecular weight. In the oxidation of unsaturated bodies, there is a disruption of the double link, and here the direct oxidation of oleic acid by aqueous permanganate gives azelaic acid, $C_9H_{16}O_4$, melting-point 108. As oleic acid dissolves in excess of caustic potash, 168 grammes of oleic acid are treated with 50 grammes of KHO and made up to the litre, and this solution on cooling decomposed by 168 grammes $KMnO_4$ in 3 litres of water, dioxystearic acid is obtained as the chief product. This acid can be converted into moniodo-stearic acid by the action of PI + H_2O and the former into stearic acid by the action of nascent hydrogen. The dioxystearic acid appears identical with iso-dioxystearic acid, obtained by Overbeck in treating oxyoleic acid obtained from dibromoleic acid and silver oxide with potash lye. Sayteff showed that oleic acid when oxidised in alkaline solution added two hydroxyl groups. The double link was replaced by the fixation added to two hydroxyl groups. He explains the reaction thus: The double link was replaced by the fixation of one atom of oxygen, and under the influence of alkalies hydration took place. Hazura formulated the following general rule from his results, viz. all unsaturated fatty acids, oxidised in alkaline solution, absorb as many hydroxyl groups as they possess free valencies and are converted into saturated fatty acids, all of which contain the same number of carbon atoms in their molecule. This rule harmonises with Fellig's researches and with Wagner's. Later Sayteff showed that the fixation of an oxygen atom by the double links cannot take place unless the permanganate first oxidises the water, so that two molecules thereof take up two hydrogen atoms and then the two resulting OH groups are fixed on both the double linked carbon atoms. Hazura contradicts this theory as the unsaturated fatty acids, when oxidised by hydrogen peroxide, must yield dioxyacids just as hempolic acid yields azelaic acid, with hydrogen peroxide. Finally, he refers to the property of alkalies for fixing $O + H_2O$. Besides he laid down the rule that unsaturated fatty acids, with three such links, also those with double links, behave in that way. Later on Holde and Marcusson advocate Wagner's theory. Ammonium oleate, in ammoniacal solution, treated with ammonium permanganate, likewise yields dioxystearic acid. In this case Hazura brought hydrogen peroxide, not in the nascent state, into play, so he held that the last objection could not be sustained. Hazura's researches on the fluid, fatty acids of drying oils are comprised in a series of contributions, which are here given in chronological order: (1) hempolic acid is referred to $C_{16}H_{28}O_2$, (2) sativic acid is $C_{18}H_{36}O_6$, and (3) linoleic acid $C_{18}H_{32}O_2$. Then the comprehensive work "On Drying Oils" completed his researches.

The Examination of Linseed Oil Fatty Acids.—Linseed oil is saponified by KHO, the soap dissolved in water, the solution neutralised by acetic acid, and precipitated by lead acetate. The lead soap is shaken up with ether, and the ethereal solution decomposed by dilute sulphuric acid, and by dilution of the ether the fluid fatty acid is obtained; 30 grammes of this fat are dissolved in 36 c.c. of aqueous potash, D = 1·27 = 29·5 per cent. KHO, and water to 2 litres, and this solution at summer temperature decomposed with energetic stirring by 2 litres of A 1·5 per cent. solution of potassium permanganate. The liquid first becomes dark green, after a time it liberates manganese peroxide, from which, after an hour's standing, the now clear fluid is separated by filtration. The alkaline filtrate contains the potassium salt of the oxyacid thus produced. It is decomposed by sulphuric acid, which causes a flocky precipitate to appear, which is filtered off and dried on porcelain plates. This acid mixture (A) is converted into the baryta salt, and then shaken with hot water. The insoluble baryta salt is decomposed by hydrochloric acid, the separated acid dried in the air, and digested with a large quantity of cold ether. On the evaporation of the ether, there only remains unoxidised linoleic acid, and dioxystearic acid, $C_{18}H_{36}O_4$. The residue insoluble in ether consists of sativic acid, $C_{18}H_{36}O_6$. The aqueous solution of baryta salts is strongly concentrated, and then decomposed by dilute hydrochloric acid. The acid separated is mostly linusic acid; there is, however, a small quantity of isolinusic acid in admixture with it from which it is separated by fractional crystallisation. The acid filtrate from A is neutralised by KHO and the 4 litres evaporated to about 300 c.c.; it is then acidulated by dilute sulphuric acid, filtered from the precipitated acid mixture, dried in the air, and dissolved in ether; only azelaic acid, $C_9H_{16}O_4$, dissolves. It is a decomposition product of linoleic acid. The portion insoluble in ether is isolinusic acid, $C_{18}H_{36}O_8$, an isomer of linusic acid. The following is a description of the properties of above acids as obtained by Hazura, together with information as to their source :—

Hazura's Acids and their Derivatives.—1. Dioxystearic acid is the oxidation product of oleic acid, $C_{18}H_{34}O_2$. Mulder's belief that linseed oil contained oleic acid was confirmed by Hazura. The constitution of oleic acid as $CH_3 . (CH_2)_7 . CH : CH (CH_2)_7 . COOH$ is firmly established. Therefore, dioxystearic acid must have the formula

$$CH_3(CH_2)_7CH . OH . CH . OH . (CH_2)_7COOH.$$

The crystalline form, according to Sayteff, is rhombic plates. Hazura at first spoke of mother-of-pearl plates, later of rhombic plates, again as blunt angled tabular crystals. Sayteff gave the melting-point at first as 132·5, later on as 136·5° C. Hazura found first 130 to 131° C., later 137° C. Gröger, who oxidised oleic acid from ox-tallow, states that he never found a higher melting for the dioxystearic acid than 130·5 to 131·5° C., and Fahrion confirms this figure as regards the dioxystearic acid from linseed oil. The latter states it can no longer be denied that different oleic acids occur in natural oils and fats. Dioxystearic acid is completely insoluble in water, freely in hot alcohol, slightly in cold alcohol, and very slightly soluble in ether. The alkaline salts are freely soluble in water, those of baryta insoluble therein. Hazura in brominating linseed oil fatty acids found that, during bromination, oleic acid yielded no crystalline derivative, only the thick dibromoleic acid. Sativic acid, $C_{18}H_{32}O_2(OH)_4$, is a tetra-oxystearic acid; it crystallises in long needles with pyramidal prisms and a silky lustre melting at 173° C. It is insoluble in cold water, carbon disulphide, ether, chloroform, and benzene, soluble in 1000 parts of boiling water, slightly soluble in cold alcohol, readily soluble in hot alcohol and glacial acetic acid. The baryta salt is insoluble in water, potassium permanganate oxidises it to azelaic acid. The four OH groups behave normally during acetylation. Finally, on treatment with iodine, followed by reduction, sativic acid yields stearic acid. Therefore, the mother substance of sativic acid must be an unsaturated fatty acid, $C_{18}H_{32}O_2$, containing four double links. Hazura called it linoleic acid. Various circumstances point to different linoleic acids occurring in different oils amongst the linoleic acid of hemp-seed oil which, according to Hazura, yields a well-crystallised tetrabromide derivative of melting-point 114 to 115° C. Linoleic acid from linseed oil yields a thick fluid tetrabrom-derivative which hardly becomes solid and melts to an amorphous mass at 98 to 100°. Finally, quite a series of tetra-oxystearic acids were obtained, the melting-point of which was below 173° C.—152 to 165. On the other hand, Thoms obtained from telfairic acid a hydroxy acid melting at 177° C. Linusic acid, $C_{18}H_{30}O_2(OH)_6$, seldom forms needles but mostly forms rhombic plates, ending in two blunt angles; melts at 203° C. It is insoluble in ether, slightly so in cold water, and more freely in hot water. But water dissolves it more freely than sativic acid. Moreover, it is slightly soluble in alcohol. The baryta salt is slightly soluble in cold water, freely soluble in hot water. With acetic anhydride it produces a hexacetyl derivative; it is a hexaoxystearic acid derived from an unsaturated fatty acid, $C_{18}H_{30}O_2$, linolenic acid. Hexabromlinolenic acid, $C_{18}H_{30}Br_6O_2$, forms needles with a melting-point of 177° C., completely insoluble in ether and acetic acid. Lately it has been prepared direct from the mixed fatty acids of linseed oil. Reformatsky regarded the hexaoxystearic acids as secondary products, although Hazura had shown previously that sativic acid on further oxidation in alkaline solution yielded no linusin nor isolinusin, but only azelaic acid and decomposition products.

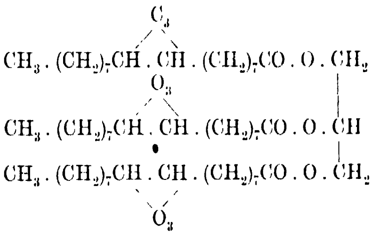
Hehner's and Mitchell's Insoluble Hexabromides.—Hehner and Mitchell, in 1898, prepared the insoluble hexabromide from linseed oil fatty acids, by bromination in ether, or acetic acid, solution. Instead of 177° C. they found the melting-point to be 180 to 181° C., and instead of the theoretical quantity of bromine, 63·31, their hexabromide yielded 61·80, or a deficiency of 1·51 per cent. No crystalline substance was obtained from the mother liquor, only a thick fluid impure tetrabromide. On boiling the impure tetrabromide with alcoholic potash the bromine was completely removed. The potassium salt of the tetrabromide, by treatment with acids, liberated a yellow viscid oil absorbing 61·63 per cent. of iodine. On reduction of the hexabromlinolenic acid with Zn + 2HCl free linoleic acid was obtained as an almost colourless oil of sp. gr.: 0·9228, iodine No. 241·6, absorbing oxygen from the air with great rapidity and turning dark brown forthwith. Hazura's linolenic acid also absorbed oxygen rapidly and could not be prepared pure, and thus could not be brought to absorb more than 245 per cent. of oxygen, the theoretical amount being 274·1. If Hazura's and Hehner and Mitchell's figures fairly agree they are both considerably below the theoretical. Brominated in acetic acid solution it is only partially converted into hexabromide, but HBr is also evolved. Later linseed oil was itself brominated in an ether solution kept cool during the operation likewise in acetic solution. It yielded about 25 per cent. of crystalline bromide, melting point 143·5 to 144°. Analysis of a mixed glyceride of hexabrom linolenin and dibrom linoleic acid, $C_3H_5(C_{18}H_{33}O_2Br_2)$, $(C_{18}H_{29}O_2Br_6)_2$.

The Preparation of Ozonides.—C. Harries began his work on the action of ozone on unsaturated compounds. He fixed a molecule of ozone on the double link, and on treating the ozonide, so obtained, with water, it decomposed with the formation of aldehydes. Harries applied the reaction to oleic acid, and by the aid of solvents produced a normal ozonide, $C_{18}H_{34}O_5$, or an ozonide peroxide, $C_{18}H_{34}O_6$. On boiling with water, it left as primary product nonaldehyde,

$CH_3(CH_2)_7.CHO$, and azelaic semi-aldehyde, $CHO(CH_2)_7CO.OH$, according to which the constitution of oleic acid is

$$CH_3.(CH_2)_7CH:CH.(CH_2)_7COOH.$$

C. Thieme also treated linoleic acid with ozone and obtained a syrupy ozonide with the approximate composition $C_{18}H_{32}O_8$. As decomposition produces only formic acid, azelaic acid and azelaic half-aldehyde were identified with certainty. When tri-olein is agitated with a solution of ozone in hexane it absorbs 3 molecules of ozone. The ozone number of tri-olein is 16·45. Calculated for $C_{57}H_{104}O_{15}$: 16·37. The tri-oleic ozonide has the following formula:—



$$\begin{array}{l} \qquad\qquad\quad O_3 \\ CH_3.(CH_2)_7CH.CH.(CH_2)_7CO.O.CH_2 \\ \qquad\qquad\quad O_3 \\ CH_3.(CH_2)_7CH.CH.(CH_2)_7CO.O.CH \\ CH_3.(CH_2)_7CH.CH.(CH_2)_7CO.O.CH_2 \\ \qquad\qquad\quad O_3 \end{array}$$

It is a thick colourless oil decomposing at 136° C., soluble in ether, acetic acid, benzene, chloroform. When heated with 20 per cent. alcoholic potash on the water-bath azeloïdic is obtained on acidulation and glycerine remains in the mother liquor. Molinari and Fenaroli have followed the matter up with the view of determining new constants for the analysis of oils and fats.

1. The iodine numbers of the ozonides of oleic and elaïdic acid and of tri-olein. The ozonides are dissolved in alcohol or a little chloroform, and an alcoholic solution of potassium iodide added. Iodine is liberated. The proportion of iodine depends to some extent on how long the mixture has been allowed to stand. For the ozonide of oleic acid 39·03 per cent. of iodine is liberated in 24 hours. To each molecule of ozone there corresponds an atom of iodine, and according thereto the iodine number of the ozonide of oleic acid is 38·45. By this method the oleic acid and tri-olein content of oils and fats may be estimated.

2. The saponification number of ozonides. The determination of oleic acid in fatty mixtures by weighing the products of decomposition nonylic acid, azeloïdic acid, does not give satisfactory results; on the contrary, better results are obtained by means of the saponification numbers of the ozonides of oleic acid and tri-olein.

Bedford's work was continued by F. Raspe, who tried to establish the constitution of linoleic acid in a manner to which no exception could be taken. Linolenic acid, prepared according to Bedford's method, was ozonised, by which it absorbed in solution 9 to 10 atoms of oxygen. Therefore, the molecule of linolenic contains 3 double links. The ozonide is a thick colourless oil, now scarcely fluid, with a peculiar smell. The ozonide peroxide is more resinous. They both behave similarly towards water. Linolenic ethylate adds, in chloroformic solution, 10 atoms of oxygen; the viscous, clear water-white product yields on decomposition with warm water, first of all azelaic acid, azelaic acid half-aldehyde, carbonic acid acetaldehyde, and a light unstable oil which gave oxalic and adipic acid on cautious oxidation. By partial decomposition with cold water, the ozonide of the *a* ester was decomposed, but nothing further was identified beyond malonic acid half-aldehyde, and malonic acid. Finally, acetaldehyde is shown to be a secondary product, derived from propionic aldehyde, so the primary decomposition products are propionic aldehyde, malonic acid, azelaic acid; that is to say, the aldehydes of both acids. He therefore ascribes the following formula to linolenic acid: $CH_3 . CH_2 . CH : CH . CH_2 . CH : CH (CH_2)_7 COOH$. Therefore, *a* and *b* linolenic acids behave similarly on ozonisation; they are therefore to be regarded as stereoisomers of the *a* acid. The A acid is the labile cis, the B acid the stabile transform.

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More recently A. Rollet has occupied himself with linoleic and linolenic acid. The first was prepared as tetrabromide, melting-point 114 to 115° C., from poppy-seed oil, from which it appears without doubt. The *b* linoleic acid of linseed oil is closely connected with the *a* acid of poppy-seed oil, as is pointed out in this research. The tetrabromide was converted directly into methyl linoleate by methyl alcohol, HCl and Zn, and by cold saponification free linoleic acid was obtained. It consists of a water-white oil, boiling-point 228° C., iodine figure 178·3 and 179·1 (instead of 181·4) d^{18}_{4} = 0·9206. Bromination only gave a 50 per cent. yield of crystallised tetrabromide. However, if linoleic acid be a single substance, then it can on bromination leave two different derivatives, both of which can be split up into two active components. On adding iodine to the oily tetrabromide no more iodine was absorbed, and on reduction it yielded not quite pure linoleic acid: boiling-point 230°, iodine figure 158·9 and 160·2, which on being again brominated no longer yielded 26·2 per cent. of crystallised tetrabromide. Possibly the fluid tetrabromide was impure. The presence of oleic acid appears not to affect the yield of solid tetrabromide as in the case of linolenic acid. On oxidation of the linoleic acid, the sativic acid produced on repeated crystallisation from alcohol melts between 156 and 169° C.; by boiling with benzol and once more crystallising from alcohol, the melting-point rises from 171 to 173° C.

Preparation of Linolenic Acid.—To prepare linolenic acid the mixed fatty acids of linseed oil are brominated in acetic acid solution and the crystalline hexabromide, melting-point 180 to 181° C., directly converted into methyl linolenate water-white oil, boiling-point 14 of oxygen. Therefore, the molecule of linolenic contains 3 double links. The ozonide is a thick colourless oil, now scarcely fluid, with a peculiar smell. The ozonide peroxide is more resinous. They both behave similarly towards water. Linolenic ethylate adds, in chloroformic solution, 10 atoms of oxygen; the viscous, clear water-white product yields on decomposition with warm water, first of all azelaic acid, azelaic acid half-aldehyde, carbonic acid acetaldehyde, and a light unstable oil which gave oxalic and adipic acid on cautious oxidation. By partial decomposition with cold water, the ozonide of the *a* ester was decomposed, but nothing further was identified beyond malonic acid half-aldehyde, and malonic acid. Finally, acetaldehyde is shown to be a secondary product, derived from propionic aldehyde, so the primary decomposition products are propionic aldehyde, malonic acid, azelaic acid; that is to say, the aldehydes of both acids. He therefore ascribes the following formula to linolenic acid : $CH_3 . CH_2 . CH : CH . CH_2 . CH : CH (CH_2)_7COOH$. Therefore, *a* and *b* linolenic acids behave similarly on ozonisation; they are therefore to be regarded as stereoisomers of the *a* acid. The A acid is the labile cis, the B acid the stabile transform.

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Glycerides of Linseed Oil.—We know almost nothing as to the principle on which, nor the manner in which the fatty acids of linseed oil are combined in the triglycerides. It was agreed at one time that all the fatty acids exist solely as triglycerides; thus oleic acid $C_{18}H_{34}O_2$ occurs in nature only in the state of triolein,

$$C_3H_5(C_{18}H_{33}O_2)_3.$$

Later on, however, a series of mixed glycerides, e.g. oleo di-stearin, $C_3H_5(C_{18}H_{33}O_2)(C_{18}H_{35}O_2)_2$, were isolated from naturally occurring fats, which were separated fractionally by long and toilsome fractional crystallisation from oil solvents. With linseed oil, owing to its great capacity of withstanding cold, this method does not succeed very well. Moreover, this capacity to withstand cold is so great that in linseed oil solid fatty acids of the mixed glycerides are in greater part prevented from crystallising out of the oil at 0° C. Henriques and Kunz set out to separate the different mixed glycerides from linseed oil in the form of halogen addition products, but Henriques' death interrupted the work, which was never resumed. Linseed oil is to-day regarded as a mixture of triglycerides, of which we know next to nothing. The mean molecular weight cannot be determined so long as the triglycerides are mixed. Now linoleic and linolenic acids form the greater part of linseed oil; their triglycerides have the molecular weight of 878 and 872, and the mean molecular weight of linseed oil must approach these figures. G. Borries was the first to make researches by Beckmann's freezing method in benzol solution. The figures 300 to 700 were found for raw linseed oil using concentration. Better results were obtained by freeing the oil from water by dry CO_2. Once more the figures were determined with strong concentration. They were 708, 674, and 644, mean 675. Norman tried to determine the molecular weight of oils by the freezing method in benzol solution and by high concentration obtained high results. By the boiling-point method the figures differed widely on strong concentration. Linseed oil gave 1182 and as low as 500·4. Ether appears to be the best solvent for the boiling-point method, A. Genthe obtaining nearly correct results, the figures being 800. F. Fokin found by the freezing method—solvents were not used—the figures 832. Evidently the molecular weight and its estimation require further investigation. Besides the triglycerides of the fatty acids, linseed oil contains other substances, but in small quantity as the glycerides of the fatty acid form 97 per cent. as a minimum, and 98 per cent. as a maximum of linseed oil. The other substances form an interesting section both from a scientific and a technical point of view.

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TABLE SHOWING THE PROPERTIES OF THE HYDROXYLATED DERIVATIVES OF THE LIQUID FATTY ACIDS OF DRYING OILS.

Name of the Original Acid.	Oleic.	Ricinoleic.	Linoleic.	Linolenic.	Isolinolenic.
Name of the corresponding hydroxylated acid	Dioxystearic acid.	Trioxystearic acid.	Sativic acid.	Linusic acid.	Isolinusic acid.
Formula of the hydroxylated acid	$C_{18}H_{34}O_2(OH)_2$.	$C_{18}H_{33}O_2(OH)_3$.	$C_{18}H_{32}O_2(OH)_4$.	$C_{18}H_{30}O_2(OH)_6$.	$C_{18}H_{30}O_2(OH)_6$.
Melting-point °C.	137.	140-142.	173.	203.	173-175.
Crystalline form (crystals in water)	—	Microscopic needles.	Long needles and pyramidal prisms.	Rhomboidal plates.	Microscopical prismatic needles.
Solubility in cold water	Insoluble.	Insoluble.	Insoluble.	Slightly soluble.	Slightly soluble.
Solubility in hot water	Insoluble.	Slightly soluble.	Insoluble.	Soluble.	Soluble.
Solubility in cold alcohol	Slightly soluble.	Slightly soluble.	Slightly soluble.	Slightly soluble.	Soluble.
Solubility in hot alcohol	Soluble.	Slightly soluble.	Soluble.	Slightly soluble.	Soluble.
Solubility in ether	Slightly soluble.	Slightly soluble.	Insoluble.	Absolutely insoluble.	Entirely insoluble.
Solubility of barium salts in cold water	Insoluble.	—	Insoluble.	Slightly soluble.	Slightly soluble.
Solubility of barium salts in hot water	Insoluble.	—	Insoluble.	Freely soluble.	Freely soluble.

Simple reasoning, therefore, tells us that the oils are those which hold the least amount of saturated acid and the largest quantity of linolenic and isolinolenic acids, which, having six valencies not satisfied, are able to absorb oxygen more rapidly than linoleic acid. Moreover, it will be observed that the classification resulting from the preceding study is in complete concordance with the facts recognised in practice and with those observed by Mulder, and also with the classification which results from the iodine absorption data.

Estimation of the Free Fatty Acids in Linseed Oil.—A perfectly neutral fat containing the exact equivalents of glycerine and fatty acid to form a pure neutral glyceride does not exist in nature. There is always a certain deficiency in glycerine, and the amount of fatty acid corresponding thereto is present in the free state. In other words, the glycerine corresponding to the free fatty acid has been split off, and oxidised to volatile compounds which have escaped. Linseed contains fat-splitting lipases, as already explained, only in a minimum quantity. Accordingly the free fatty acid content of linseed is correspondingly small. Mulder's statement that fresh linseed oil is perfectly neutral cannot be accepted.

Pure samples of raw linseed oil, unless oxidised or thickened or very old, contain only small amounts of free fatty acid, whilst if sophisticated with rosin oil, which abounds in free rosin acids, the percentage acidity may be much increased. In the distillation of rosin there is a good deal of vesicular carrying over of unchanged rosin in the train of the vapour of rosin oil; hence the marked acidity of the latter unless the rosin oil has been well refined by redistillation over caustic soda lye. Rosin itself consists of a certain organic acid which very probably differs slightly in different samples which have been described by different observers as abietic, pimaric, etc., but all of which are referred to one single acid by Skateloff, viz. sylvic acid. Rosin has an average acid number of 164, so that 5 per cent. of rosin in an oil would increase the acid number by 8 at least. But the natural acidity of genuine linseed oil increases with age by the accumulation of the fixed oxidation products of the oil. The older the linseed from which the oil is expressed, the greater will be the free fatty acid content of the expressed oil. Moreover, during the pressing of fresh seed, even owing to the practice of forewarming the seed, a slight increase in the free fatty acid content may occur. So that although a high acidity might indicate the presence of rosin acids, and hence of rosin oil or free rosin, yet it would not be safe to come to a decided conclusion without confirmatory evidence. A portion of the acidity may even be due to free sulphuric acid used in refining the oil, but any appreciable proportion would point to unmitigated carelessness on the part of the refiner in washing, seeing he hardly ever uses more than about 1 per cent. of acid. The actual amount of acidity due to sulphuric acid is estimated by repeatedly boiling a known quantity of the oil with water until free from acidity, collecting the wash waters, concentrating, and, after cooling, adding neutral potassium iodide and iodate and titrating the liberated iodine, if any, with sodium hyposulphite. The free iodine found is calculated to caustic potash, KHO, and deducted from the potash required to neutralise both the sulphuric acid and the organic acids present in the sample. The remainder gives the free organic acids, which consist of the fatty acids from linseed oil alone if the sample be pure, but if adulterated it may represent in addition the acidity due to the presence of rosin added either as such or in the form of rosin oil. The total free acid is determined as follows: From 5 to 10 grammes of the oil are weighed into a flask and 50 to 100 c.c. of alcohol added; if methylated spirit be used it must be previously neutralised, as it is always acid. Heat on the water-bath, shake, cool, and titrate with deci-normal alkali; add a few drops of phenol-phthalein. The result is calculated to milligrammes of caustic potash, KHO, per gramme of oil.

The free fatty acid may be quantitatively separated as the sodium salt by treating the oil with excess of dry sodium bicarbonate, and extracting the mixture with petroleum ether. The neutralised fat is dissolved, and the resultant soap can be separated as fatty acid by hydrochloric acid. But the method is not applicable to linseed oil owing to its tendency to oxidise.

The method of calculation may be carried out as follows:—

Suppose 9·525 grammes of linseed oil to require 4·5 c.c. of deci-normal KOH.

$$\text{Then} \qquad \frac{4{\cdot}5 \times {\cdot}0056 \times 1000}{9{\cdot}525} = \text{say } 2{\cdot}6 \text{ free acid value.}$$

It is sometimes desirable to report the results in terms per cent. of oleic acid. Such is approximately obtained by simply dividing the ascertained free acid value by 2, thus:—

Let 2·6 equal free acid value.

$$\text{Then} \qquad \frac{2{\cdot}6}{2} = 1{\cdot}3 \text{ per cent. oleic acid.}$$

This method of calculation is ample for a general report.

The acidity of linseed oil expressed as oleic acid, according to Nordlinger, varies from 0·41 to 4·19. McIlhiny gives an acid value of 3·0 as the usual figure, which equals oleic acid 1·51. A very old sample gave 7·1. Mills allows a maximum acid value of 10. It will be readily understood that boiled oil gives higher acid figures than raw oil. Weger allows as high an acidity as 12, and in very much thickened oils he allows 30. However, free rosin may be introduced by fused metallic rosinates, the so-called "resinates," with the accent on the *e*. The acid figure of boiled oil, says

McIlhiny, is usually below 5, but it is more uncertain than the raw oil. A figure above 10 is in his opinion undoubtedly due to the presence of rosin, which seems rather a dogmatic dictum. The acid value of rosin varies from 145 to 180, and its detection is facilitated by its giving both a high bromine substitution figure as well as an addition figure. But the safest method is to estimate it quantitatively by one or other of the methods adopted in soap analysis, such as Gladding's or Twitchell's. But the process often recommended, to exhaust the oil with *pure alcohol* and then to add an alcoholic solution of basic acetate of lead, is not reliable, as linoleate of lead formed from the free linoleic acid does not dissolve in alcohol to any very appreciable extent more than the rosinate of lead. The operator is thus thrown back upon the character of the precipitate—always a very unreliable indication.

The Free Acidity of Linseed Oil Increased on Oxidation of Linseed Oil; the Percentage of Oxyacids as a Measure of Oxidation.—Bauer and Hazura found that the acid number of two samples of linseed oil, kept for four or five years in loosely stoppered flasks, had increased by 8·9 and 12·1. Fahrion uses the oxyacid content as a measure of the extent of oxidation. In a sample of linseed oil, over one year old, which had not been heated in any way but kept in a glass vessel not quite full and often opened to take out samples, Fahrion found an iodine value 151, together with 6·5 per cent. of oxyacids. As a test this oil was heated for four hours at 110° C., when the iodine number sank to 136·1, whilst the oxyacid content rose to 11 per cent. Thomson and Ballantyne left linseed oil in an open vessel with constant stirring, exposed to the air for six months. The density rose from 0·9325, its original oil, to 0·9331 at end of first month, to 0·9385 at end of six months; the iodine number sank from 173·5 to 166·2.

TABLE SHOWING MONTHLY INCREASE IN DENSITY IN OILS EXPOSED TO AIR IN UNCORKED BOTTLES FROM ONE MONTH TO SIX MONTHS, THE BOTTLES BEING SHAKEN EVERY MORNING. (THOMSON AND BALLANTYNE.)

Oil.	Density, Original.	Densities at End of Each Month.					
		1.	2.	3.	4.	5.	6.
Olive . .	0·9168	0·9187	0·9193	0·9208	0·9215	0·92 7	0·9246
Castor . .	0·9679	0·9681	0·9691	0·9700	0·9700	0·9685	0·9683
Colza . .	0·9168	0·9183	0·9172	0·9185	0·9184	0·9200	0·9207
Cotton-seed .	0·9225	0·9237	0·9241	0·9261	0·9278	0·9304	0·9320
Arachis . .	0·9.09	0·9213	0·9221	0·9233	0·9239	0·9256	0·9267
Linseed . .	0·9325	0·9331	0·9336	0·9353	0·9359	0·9372	0·9385

TABLE SHOWING THE FREE ACID CONTENT OF VARIOUS SAMPLES OF LINSEED OIL.

Authority.	No. of Samples.	Origin.	Acid No.	Free Fatty Acid, Per Cent.	Remarks.
Nordlinger . .	10	—	—	0·41-4·19	Technical oil, Average 1·57
Haselhof . . .	3	—	—	0·07-0·27	From pure seed fresh pressed.
Lewkowitsch . .	4	3 Russian, 1 Indian	1·3-1·8	—	—
Schestakoff . .	11	Russia	—	0·55-4·33	—
Tomarchio . .	6	Various	—	0·35-1·20	—
American Committee	4	U.S.A.	1·1-3·3	—	—

Estimation of the Mixed Fatty Acids of Linseed Oil.—To calculate these it is not sufficient to take the chief ingredients of linseed oil in the form of their respective triglycerides, formulating these as $C_3H_5(C_{18}H_{32}O_2)_3$ and $C_3H_5(C_{18}H_{30}O_2)_3$. These formulæ calculated for both glycerides give 95·7 per cent. for linoleic acid and 95·67 for linolenic acid, and the mixed fatty acid content of linseed oil must therefore closely approach these figures. Mulder found similar figures after the removal of the volatile fatty acids; he estimated the fixed fatty acids thus: he saponified linseed oil by aqueous lye, decomposed the soap by dilute H_2SO_4, filtered off the fatty acids, washed them with water dissolved in alcohol, evaporated the solution and dried the residue at 100° C. (212° F.). In a linseed oil prepared by himself he found 95·4 per cent., in a commercial oil, 95 per cent. of mixed fatty acids. The results were rather low. Mulder heated myristic and palmitic acids on tin plates for six hours at 80° C., and found that they did not change in weight, whilst linoleic and linolenic acids increased 12·1 per cent. On another occasion Mulder found that linoleic acid increased in weight on heating. That this increase cannot be neglected was shown by R. H. Tatlock of Glasgow. He heated the mixed fatty acids of linseed oil for varying periods at 90° C. and found after 24, 48, 96, 120 hours an increase in weight by increments of 1·25, 1·23, 0·42 and 0·19.

Mulder's method described above was modified by Hehner. He dispensed with solution in alcohol, collected the fatty acids directly on the filter and dried. The percentage yield of fixed fatty acids turned the Hehner number. In the case of drying oils the Hehner process was but little practised, as in the draining of the fatty acids on the filter paper auto-oxidation was started.

Fahrion prepares the mixed fatty acids of linseed oil thus: N/2 alcoholic potash is used for saponification. To prepare it 120 grammes of pure KHO are dissolved in their own weight of water, and the solution made up to a litre with 96 per cent. alcohol thoroughly mixed by agitation, and filtered next day through glass wool or asbestos, or through strong filter paper. It is advisable to ascertain the proportion of the very pure commercial electrolytic potash lye, which contains over 70 volumes per cent. KHO, to be mixed with 96 per cent. alcohol and filtered next day. A less quantity of lye will, of course, be used. Saponification is best effected in a porcelain basin of 100 c.c. capacity, the outside of which is unglazed, which can be conveniently put on the plate of the balance scales. In another basin 2 to 3 grammes of linseed oil are weighed out, 10 c.c. of the above lye added and warmed with constant stirring on the water-bath, eventually on the wire gauze, until the alcohol is completely expelled. It is then made certain that complete saponification has taken place. The soap is completely dissolved in 50 c.c. warm water, and this solution transferred to a separating funnel. When cold, 25 c.c. petroleum ether, completely volatile at 75° C. (167° F.), is first added, then 10 c.c. of 10 per cent. HCl, well agitated, and let stand till morning, when the acid aqueous solution is run off, and the petroleum ether solution brought on to a tared porcelain basin, which is best only half-filled. It is brought on to a gently boiling water-bath and the petroleum ether evaporated. When that is effected, the water-bath is brought to a strong boil and the basin left thereon for an hour. When the temperature of the bottom shows 90° C. it may safely be taken that the last trace of solvent has been evaporated. The basin is wiped with a soft towel, dried forthwith, and completely cooled, best on a metal under-surface, then weighed. Fahrion found 95 to 96 per cent. by this method, which is rather high, as the oxidation of the unsaturated fatty acids is incomplete. The Hehner value of the non-drying oils comes out high, hence it is to be regretted that only slight information is available as to the Hehner value of linseed oil. Lewkowitsch gave 95·5 as an average.

After Mulder, thirty years elapsed without further progress on the above question. We have now to deal with so-called soluble driers, by which boiled oils may be made, in which the metallic content can be adjusted to a nicety. But, away back in 1895, Amsel declared that pure linseed oil dried in 3 days, with 5 per cent. "drier" in 24 hours. Lippert rightly charged Amsel with making a mistake, because pure linseed oil, in drying, varied with the surrounding circumstances, and also in the case of the drier the nature of its metallic content intervenes. He then made two solutions of precipitated manganese linoleate in turpentine, one with 9·9 grammes to the litre, the other with 2·8 grammes manganese to the litre, mixed 25 c.c. linseed oil with 5 c.c. of the above solution and spread the boiled oil so obtained, which contained from 0·014 to 0·049 per cent. manganese, on tin plates. The first dried in 24 hours, the second in 48 hours. Weger therefore decided that the conclusion from this experiment was that within limits the more drier, the quicker the drying. There are, however, three things which may happen :—

1. The drying capacity rises proportionately with the amount of drier.
2. He gives a maximum capacity for each drier.
3. On exceeding the maximum the drying capacity lowers.

Mean Molecular Weight of the Mixed Fatty Acids of Linseed Oil. —Linseed oil fatty acids dissolve freely in alcohol. An alcoholic solution of these acids can therefore be titrated with standard soda and the mean molecular weight calculated from the result. If x be the molecular weight, then 1 litre contains x grammes of oil; when, therefore, a grammes (or at the most three) uses b c.c. $x = \frac{1000\,a}{b}$.

Piles of acid numbers of the mixed fatty acids are given in the special literature. The titration results are calculated to milligrammes of KHO for 1 gramme of fat.

The following formula shows the relationship between the two :—

$$\text{Molecular weight} = \frac{5600}{\text{acid number}}.$$

The molecular weight of linolenic acid is 278, that of linoleic acid 280. The molecular weight of oleic acid is 282. Its presence increases the mean molecular weight; again, the unsaponifiable, consisting of neutral bodies, with the solid fatty acids, palmitic 228 and myristic acids 256, lower the mean molecular weight. It will readily be seen that as the mean molecular weight of linseed oil fatty acids is between 275 and 280, its acid number must lie between 200 and 204. In practice, the acid number is greater than the mean molecular weight.

Tortelli and Pergami acid No. = 194·6 ; molecular weight = 288·2
Fahrion „ „ = 193·2 ; „ „ = 289·9
Schestakoff „ — ; „ „ = 303

As to the above figures it is to be noted that during heating of the linseed oil fatty acids a portion of the carboxyl groups is changed. Formation of acid anhydrides cannot occur; they are formed below 100° C. and are unstable in contact with water. The formation of lactones is improbable, as oleic acid $C_{18}H_{34}O_2$ is only converted into stearo-lactone $C_{18}H_{34}O_2$ by acting on it with powerful reagents, e.g. concentrated sulphuric acid or zinc chloride. Finally stearo-lactone melts at 51° C., and undergoes no change on saponification as oxystearic acid is not present. However, neutral bodies are formed which lower the acid number by the saponification of the remainder of the original acid. The mean molecular weight is best determined as follows: The fatty acid is treated with excess of alcoholic potash and the excess determined. A normal solution is generally used which can be made by diluting a strong solution of its own volume of alcohol. About 3 grammes of fatty acid are warmed with 25 c.c. of the above solution; when cold, phenol phthaleïn is added and the solution titrated back with normal HCl.

The strength of the alkaline solution is adjusted by a blank experiment. The difference between both tests gives the alkali consumed, which, converted into mgs. KHO for 1 gramme of fatty acid, gives the saponification number. Compared with the acid number the results are identical but generally higher, and the corresponding molecular weight of the inner half from the above data = 275 to 280.

Tortelli and Pergami, saponification number 201·8; molecular weight 277·9. Fahrion saponification number 202·5; molecular weight, 276·5.

TABLE OF THE ACID NUMBER AND THE MEAN MOLECULAR WEIGHT, THE SAPONIFICATION NUMBER AND THE MEAN MOLECULAR WEIGHT OF THE MIXED FATTY ACIDS OF THREE DIFFERENT LINSEED OILS.

Sample No.	Acid No.		Saponification No.	
	Acid No.	Mean Molecular Weight.	Saponification No.	Mean Molecular Weight.
I.	201·8	278·0	199·8	280·9
II.	194·7	288·1	199·8	280·7
III.	195·2	287·4	199·0	281·9

Lewkowitsch has apparently found in two instances higher results for the mean molecular weight of the acid number of the fatty acids than for their saponification number, which on the face of it seems absurd.

With a change in weight reaction occurs which reduces the acid number. However, during heating of linseed oil fatty acids in the air, another reaction supervenes which results first in an increase in weight, and by very prolonged heating the weight decreases. The second reaction is auto-oxidation. Owing to absorption of oxygen from the air a small amount of oxyacids is formed. Finally comes the question of another source of error due to the carboxyl still containing weak acid groups which on neutralisation do not enter into the reaction only on saponification. Fahrion has shown that the above saponification number is too high and the corresponding mean molecular weight 276·5 is too small, the correct molecular weight being 279·7. Moreover, in the separation of linseed oil fatty acids from linseed oil by treatment with alcoholic potash, the glycerine is quite indifferent to the alkaline lye, so that in estimating the saponification number of linseed oil itself, it suffices to determine the number of milligrammes of KHO required to neutralise the mixed fatty acids from 1 gramme of linseed oil. Naturally this figure is lower than the saponification number of linseed oil fatty acids by about 4 to 5 per cent., as linseed oil contains only 95 to 96 per cent. of fatty acids.

The saponification number of linseed oil may be determined quite similarly to that of the linseed oil fatty acids, only gentle heating in this case is not used. About 3 grammes of oil are boiled with 25 c.c. of about normal alcoholic potash, until the solution is completely taken up and heating continued for 1 minute; when cold the excess of alkali is titrated back with normal HCl. The dissociation of the soap must be guarded against, and the alcoholic strength of the solution should not sink below 50 per cent.; when during boiling the alcohol becomes dilute it must be strengthened by fresh alcohol.

TABLE OF SAPONIFICATION VALUES OF MIXED FATTY ACIDS OF LINSEED OIL COLLATED BY FAHRION.

Authority.	Saponification No.
F. Filsinger, Chem.-Ztg., 1894, **28**, 1006	187·8-192·3
W. Thörner, Chem.-Ztg., 1894, **28**, 1151	190 -192
H. Amsel, Zeitschr. f. angew. Chem., 1895, **8**, 75	188 -190
R. Henriques, Zeitschr. f. angew. Chem., 1895, **8**, 722	193·5-195·3
J. Lewkowitsch, Chem. Rev., 1898, **5**, 29	192·9-194·3
Tortelli und Pergami, Chem. Rev., 1902, **9**, 182	189·8
J. van Itallie, Pharm Weekblad, 1903, **40**, 106	192·9-193·5
Tolman u. Munson, J. Amer. Chem. Soc., 1903, **25**, 954	191·7
C. Niegemann, Chem.-Ztg., 1904, **28**, 97	187 -196
Thomson und Dunlop, Analyst, 1906, **31**, 281	191·4-192·8
American Committee	190·4-192·2

TABLE SHOWING THE MELTING-POINT AND SOLIDIFYING-POINT OF THE MIXED FATTY ACIDS FROM LINSEED OIL.

Authority.	Solidification-point °C.	Melting-point °C.
Allen	17·5	24
Hubl	13·3	17
Lewkowitsch	19-20·6	—
Livache	21 0	23·0
De Negris and Fabris	16-17	20-21
Thorner	13·5	17
Tolman and Munson	—	19 2

The specific gravity of linseed oil fatty acids is not often determined. Their melting-point being above 15° C. requires a higher temperature. Their expansion coefficient is unknown, naturally the correction figures for linseed oil do not apply to the fatty acids.

Recent researches have shown that the quite fresh fatty acids are far more readily oxidised than linseed oil itself.

Allen $d\frac{15{\cdot}5}{15{\cdot}5} = 0{\cdot}9233$

Bearn $d\frac{15{\cdot}5}{15{\cdot}5} = 0{\cdot}9158.$

Archbutt $d\frac{100}{100} = 0{\cdot}8925.$

Thorner $d\frac{100}{100} = 0{\cdot}889.$

CHAPTER VII.

THE TESTING OF LINSEED OIL.

Determination of Rosin Oil and Mineral Oil in Linseed Oil by Saponification and their Extraction from the Solution of the Resultant Soap by Ether.—Five grammes of the sample to be tested for the presence of mineral oil (indicated by low specific gravity and by the fluorescence of the sample), or for the presence of rosin oil (indicated by the high specific gravity of the sample and by its fluorescence), or for the presence of both these hydrocarbide oils, are saponified with 25 c.c. of alcoholic potash, 80 grammes of caustic potash to the litre of alcohol in a capacious porcelain basin, care being taken to apply heat very cautiously at first, as the mixture froths much and is apt to take fire.

A perfectly clean flat copper plate should be kept ready to cover the top of the porcelain basin to extinguish any such fire instantly.

When frothing has ceased a greater heat may be applied, but in bringing the soap to dryness at the end, care must be taken to avoid charring or overheating, which might distil off some of the rosin oil, etc. The operation may be done very well on the sand-bath with care.

The resultant soap is dissolved in the basin in 50 c.c. of boiling water and transferred to a separating funnel of about 200 c.c. capacity, using about 20 to 30 c.c. of water for rinsing out the basin. After cooling 50 c.c. of ether are added, and the solution and ether thoroughly shaken in the funnel. The funnel and its contents are allowed to stand, when the ether separates out as an upper layer, containing the greater portion of the rosin oil in solution. A few drops of alcohol hasten the separation, but the use of alcohol is an expedient which should be resorted to as little as possible, and as

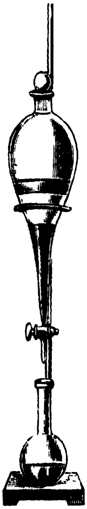

FIG. 42.—Separating funnel showing separation of the ethereal solution of rosin oil from the soap made from linseed oil containing rosin oil.

little alcohol as is absolutely necessary should be used. The soap solution is then run off through the stop-cock whilst the ethereal solution is run into a separate flask. The soap solution is then returned to the funnel and again agitated with ether and the process repeated until the soap solution cedes no more rosin oil, etc., to the ether. Three or four extractions as above may be necessary before the ether floats to the top as a colourless layer. The ethereal solutions are united and washed with a small amount of water to eliminate any dissolved soap or free alkali. The ether is distilled off on the water-bath and the residue dried and weighed. The soap solution is saturated with ether, and when ether is clear it may pay to recover it by distillation. In a works laboratory the greater part of the ether may be driven off by using several beakers of boiling water brought from the waste steam pipes, and if the laboratory lights are all out there is no danger of explosion. Nine-tenths of laboratory explosions are ether explosions. (Ether vapour will explode or burn 12 feet away from its source, and the flame or explosion strike back to it.)

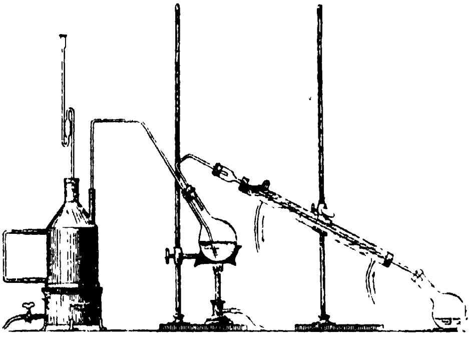

Fig. 43.—Distillation apparatus.

Fig. 43 shows an apparatus fitted up for fractionally distilling an oil varnish by the aid of steam so as to carry over the unchanged turps in the train of the steam. The volatile portion of the oil varnish is thus separated from the two other ingredients forming the fixed portion which cannot be distilled without decomposition: these consist of (*a*) fused resin dissolved in (*b*) linseed oil, and drier, possibly a fused linoleate, or a fused rosinate, or a mixture of both combined with either lead oxide or manganese oxide, or both.

The Percentage of Spirits of Turpentine, and other Volatile Oils in Linseed Oil, etc.—Benzene and other solvents, etc., spirits of turpentine, coal-tar benzene and its homologues; shale naphtha and petroleum naphtha, shale spirit deodorised or otherwise, are readily detected in linseed oil, whether raw or boiled, and whether they be present i comparatively small or relatively large proportions, by their characteristic smells, which are accentuated by placing the oil in a tes tube or other vessel so as to half fill it, and then dipping the tub into boiling water after having corked it up. On releasing and removing the cork the characteristic odour of the individual volatil solvent present will make itself felt. Moreover, the greatly diminished flash-point will also show substances of this nature, which ar also revealed by the low specific gravity if present in any quantity To estimate the volatile oil quantitatively about 300 grammes ar heated by a bath of molten paraffin wax or by an air-bath to abou 130° C. in a flask capable of being connected with a vessel in whic steam is generated. It therefore has a cork fitted with an inlet tub reaching nearly to the bottom of the vessel B, a thermometer inserte into the oil, and a tube for leading the steam and the vapour of spirit of turpentine, etc., which it carries in its train to a Liebig's condenser The distillate C collected in the receiver D will consist of two layers, a upper one of spirits of turpentine, etc., floating on a layer of water The former is separated from the latter by a separating funnel, and weighed or measured. The layer of condensed water retains trace of the volatile oil, but so small that it may very well be neglected. McIlhiny found it to be about ⅓ of 1 per cent.

Petroleum spirit may, it is claimed, be separated from spirits o turpentine by treating the mixture with fuming nitric acid. Petroleum spirit remains unattacked, but spirits of turpentine is converted int substances which can be dissolved in water, and thus eliminated from the mixture, leaving a residue of more or less pure petroleum spirit. A measured amount of the distillate is run into 300 c.c. of fuming nitric acid (very slowly, drop by drop) contained in a 250 c.c. flask attached to a reflux condenser. As each drop of the oil falls on the fuming acid a very violent reaction ensues, and the flask should be immersed in cold water to keep it cool, and it should be agitated from time t time. When the whole of the volatile oil to be treated has bee added the flask is let stand until all action has ceased, when it contents are run into a separating funnel (Fig. 42) and repeatedl washed with hot water, which eliminates the products produced b the interaction of the spirits of turpentine and the fuming nitric acid such products being soluble in water. The residual petroleum spiri is now measured and brought to per cent. by volume of the distillat and then to per cent. of the original oil. However applicable thi method may be to petroleum naphthas consisting of pure paraffinoid hydrocarbides, it is on the face of it wholly inapplicable to *inter alia* shale naphtha, largely consisting of members of the ethylenic serie of hydrocarbides, the so-called "olefins," all of which are readily attacked by nitric acid. This is a point which seems to have been unaccountably overlooked by those writers who recognise and quot the above method as an efficient one for separating petroleum spiri from spirits of turpentine. It is very evident their knowledge is mere book knowledge, and poor at that!

Mr. Phillips, late chemist to the Great Eastern Railway, separated turps from linseed oil by distilling in an atmosphere of coal gas. But this method seems to the author to be open to several objections. There is no saying whether any, and if so what, substances might not be dissolved from the coal gas by turps and carried forward in the train of its vapour. The determination of volatile substances in linseed oil has been made the subject of an inquiry by the U.S. Bureau of Standards, and the author's recommendation of the McIlhiny process in this treatise was quoted by the Bureau.

Saponification Value or Koettstorfer Figure of Linseed Oil.—This is defined as the number of milligrammes of caustic potash, KHO, required to completely saponify 1 gramme (i.e. 1000 milligrammes) of linseed oil. Or, to use British units, it is the number of grains of caustic potash required to saponify 1000 grains; or, for that matter, the number of tons of caustic potash required to saponify 1000 tons of oil. Divided by 10, the saponification number again gives the number of pounds of caustic potash required to saponify 100 lb. of oil. It is really a very simple matter, but the use of foreign, if scientific, units (grammes per litre when lb. per 100 gallons has the same meaning and effect) tends to render it unintelligible to the non-scientific layman.

Reagents.—(1) Standard hydrochloric acid, the strength of which is expressed in terms of caustic potash, KHO. The semi-normal acid is the most suitable; such an acid contains in every litre, that is, in every 1000 c.c., 18·25 grammes of anhydrous hydrochloric acid, HCl. The pure solution of hydrochloric acid is diluted by referring to the tables of density with distilled water until this strength is reached; its exact strength may be determined by estimating its chlorine as chloride of silver, AgCl. The solution may also be standardised by titration with a known weight of pure, dry, freshly ignited sodium carbonate, Na_2CO_3, every 106 grammes of which are equal to 112·2 grammes of caustic potash, KHO. The hydrochloric acid, to be perfectly semi-normal, should be so diluted that 0·265 gramme of pure anhydrous sodium carbonate require 10 c.c. of the diluted acid for neutralisation. The exact strength of the standard hydrochloric must always be known in terms of caustic potash, which, when exactly semi-normal, is 1 c.c. = 0·02805 KHO.

Alcoholic Potash Solution.—This need not be of a very exact predetermined strength, but should approach, as far as practicable, the semi-normal, so that 1 c.c. of the alcoholic potash solution neutralises 1 c.c. of the semi-normal acid. To 1 litre of alcohol 30 to 40 grammes of caustic potash are added, or rather 75 c.c. of an aqueous solution of caustic potash of 45° Baumé or 90 c.c. of 36° Baumé are run into a litre of alcohol, and the whole allowed to stand and filtered through a ribbed filter, or decanted after clarifying into a bottle with a straight neck and corked with an india-rubber stopper, through a hole in which a 25 c.c. pipette passes, the end of which is closed by a piece of india-rubber tubing and a small clip. It is not advisable to prepare too much of the solution as it is not stable. The alcohol should be the purest obtainable (if methylated spirit be alone available it should be purified by redistilling it over soap). The alcohol should not become brown, the colour of rum, or cod oil in the process. A yellowish tint does not interfere with the titration.

Process.—From 1·5 to 2 grammes of the filtered or otherwise prepared oil are weighed exactly into a 150 to 200 c.c. flask, then 25 c.c. of the alcoholic potash solution measured out by the pipette, in the stopper of the bottle, are added. It is not necessary to rigidly measure out 25 c.c. exactly, but precisely the same quantity must be taken for each experiment. After the contents of the pipette have drained it is better to grasp tightly the bulb of the pipette in the palm of the hand and "squeeze," as it were, the remainder of the liquid out of the pipette; the heat of the hand expands the air inside the pipette, and the top aperture being closed by the finger, the expansion of the air causes all the liquid, except the merest traces, to be forced out of the mouth of the pipette. A similar flask, with 25 c.c. of alcoholic potash, is used as a blank experiment, and both fitted with reflux condensers are heated on the water-bath simultaneously for half an hour, and afterwards cooled. Two to three drops of phenolphthalein are then added to each flask, and the contents titrated with the semi-normal hydrochloric acid. The difference between the blank flask and that containing the oil is calculated into potash; or, the volumes of alkaline solution added being equal, the difference found is potash used up by the oil. 1 c.c. of acid = 0·02805 gramme of KHO, and this factor multiplied by the number of c.c. of acid consumed gives a number which, × 1000 ÷ by the amount of oil taken, gives the number of milligrammes of caustic potash consumed by 1 gramme of oil, and this figure is generally called the Koettstorfer figure or saponification value.

EQUIVALENT WEIGHTS OF CAUSTIC AND CARBONATED ALKALI.

Potash Alkali.	Formula.	Molecular Weight.	Equivalent Weight.	Soda Alkali	Formula.	Molecular Weight.	Equivalent Weight.
Caustic potash .	KHO	56·1	112·2	Caustic soda .	NaHO	40	80
Anhydrous potash	K_2O	94·2	94·2	Anhydrous soda .	Na_2O	62	62
Potassium carbonate . .	K_2CO_3	133·2	138·2	Sodium carbonate	Na_2CO_3	106	106
				Soda crystals .	Na_2CO_2+10aq	286	286

The strength of commercial alkali is always expressed in per cent. of anhydrous alkali. as in the second horizontal line: if the caustic potash be pure it contains 94·2 per cent., and knowing the saponification value of the oil and the percentage of anhydrous potash in the alkali being used, the calculation of the amount required to saponify any given oil or rosin whose saponification value is known is a simple matter.

Analytical Examples.—(1) Where the acid and alkali are both semi-normal, and (2) where neither are semi-normal.

Example 1.—Linseed oil taken	1·75 grammes.
½ Normal alcoholic potash taken .	25 c.c.
½ „ acid used in back titration	13 c.c.
	12 c.c.

Each c.c. semi-normal acid = 0·02805 gramme KHO.

12 „ „ „ „ = 0·33660 „ „

0·3366 gramme KHO × 1000 = 336·6 milligrammes KHO.

$$\frac{336 \cdot 6}{1 \cdot 75} = 192 \cdot 4 \text{ milligrammes KHO.}$$

It therefore took 192·4 milligrammes of caustic potash to completely saponify 1 gramme of the linseed oil in question.

Example 2.—Benedikt and Ulzer give the following example: 2·012 of oil were saponified with 25 c.c. of alcoholic potash and 9·65 c.c. of standardised hydrochloric acid were used in back titration. 25 c.c. of the alcoholic potash = 22·5 c.c. of the standard hydrochloric acid. Again 1 c.c. of the standard hydrochloric acid = 0·0301 gramme caustic potash, KHO. There was used in saponification of the oil, therefore, an amount of caustic potash equal to 22·5 − 9·65 = 12·85 c.c. of test acid, hence 12·85 × 0·0301 gramme × 1000 = 386·8 milligrammes, ÷ 2·012 grammes, amount of oil taken, = 192·24 milligrammes for 1 gramme of oil. The oil tested therefore had the saponification value of 192·24.

The saponification value of linseed oil is higher than that of most oils, but it can only be regarded as affording an indication of purity. Even a comparatively high saponification value is no guarantee that the oil is not adulterated with non-drying oils which approach it very closely in this respect; neither is it a guarantee that unsaponifiable substances, such as hydrocarbide oils, are absent. The only way to determine the absence or presence of these is to actually separate them out (and weigh them) by the saponification process first introduced by Thomson, and afterwards elaborated by Allen, which consists in first saponifying the oil and then extracting the hydrocarbide oils from the aqueous solution of the resultant soap by ether (see pp. 103-104).

When the saponification number is as low as from 180 to 185, then adulteration with rosin oil or mineral oil is to be strongly suspected, and [illegible] falls lower than 175 their presence is certain (Weger). It may [illegible] be demanded of a raw oil that its figure shall not be lower than 187 and of a boiled oil not lower than 186 (McIlhiny). The high temperature used in the old-fashioned process of oil-boiling reduced the saponification value much greater than the much lower temperature now used with modern processes, in which readily soluble driers, rosinates, and linoleates are used. The amount of metal introduced into the oil in the form of a metallic rosinate or linoleate is so small as not to produce any very appreciable effect on the saponification value, and some of the boiled oils now in the market have almost as high a saponification number as that of the raw oil.

The Ester Number of Linseed Oil.—It is the difference between the acid number and the saponification number. The two former therefore added together give the saponification number. The estimation of glycerine may be dealt with here. One molecule of glycerine (molecular weight = 92) combines with 3 molecules of fatty acids, so the formula $\frac{\text{acid number} \times 92}{3 \times 56}$ gives the amount of glycerine in 1 gramme of oil. Hence the ester value shows the percentage of glycerine in linseed oil as 5·5 per cent. If we take 191 as the mean saponification number, the acid number as 3, then the mean ester number is 188 and the mean glycerine content as 10·4 per cent.

Iodine and Bromine Value of Linseed Oil.—Linseed oil consists largely of unsaturated glycerides, the fatty acids of which combine by *direct addition* with 2, 4, or 6 atoms of bromine or iodine. Rosin, rosin oil, and mineral oil do so only to a slight extent, and, menhaden oil excepted, no other adulterant to as great an extent as linseed oil itself. *Direct halogen addition* is not the only action; there is another in which one-half of the halogen combines with the oil and the other half combines with hydrogen, which the first half of the halogen has displaced from the oil. The halogen has formed a *substitution* compound with the oil. If the hydrogen of glycerides can be but very sparingly replaced by bromine or iodine, it is not so with rosin, rosin oil, and mineral oils. In fact though rosin and rosin oil absorb large amounts of bromine they do so by substitution and not by direct addition, and with American petroleum oils substitution compounds bulk largely in the absorption.

The halogen absorption of oils is generally determined by Hübl's or Wijs' method. It affords valuable data as to purity of any sample of linseed oil. But it does not differentiate between absorption by (1) addition and (2) substitution. It fails to discriminate between rosin and linseed oil, the absorption figures of both linseed oil and rosin being somewhat close.

Reagents.—(1) *Iodine Solution.*—Dissolve 25 grammes of pure iodine in 500 c.c. of 95 per cent. alcohol. Dissolve 30 grammes of mercuric chloride corrosive sublimate in 500 c.c. of 95 per cent. alcohol. The last solution, if necessary, is filtered, and then the two solutions mixed. The mixed solution should be allowed to stand 12 hours before using. Iodine chloride is formed according to the following equation: $4I + HgCl_2 = HgI_2 + 2ICl$. The latter calculated to iodine absorption per cent. of the oil or fatty acid gives the iodine number. (2) *Decinormal Hyposulphite of Sodium Solution.*—Take 24·6 grammes of chemically pure hyposulphite of soda freshly pulverised as finely as possible and dried between filter or blotting paper. Make this up to 1000 c.c. at the temperature at which the titrations are to be made. (3) *Starch Paste.*—1 gramme of starch boiled in 200 c.c. of distilled water for 10 minutes and cooled to room temperature. (4) *Solution of Iodide of Potassium.*—100 grammes of iodide of potassium dissolved in water and made up to 1 litre. (5) *Solution of Bichromate of Potassium.*—Dissolve 3·8657 grammes of chemically pure bichromate of potassium in distilled water, and make the volume up to 1 litre at temperature at which titrations are to be made. (6) *Chloroform.*—This should be pure and should not affect titration results of iodine solution after 3 hours' standing.

Manipulation—Standardising the Sodium Thiosulphate Solution.—Run 20 c.c. of the potassium bichromate solution to which has been added 10 c.c. of the solution of potassium iodide into a glass-stoppered flask. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow colour of the liquid has almost disappeared. Add a few drops of the starch paste and with constant shaking continue to add the sodium thiosulphate solution until the blue colour just disappears. The number of cubic centimetres of thiosulphate solution used multiplied by 5 is equivalent to 1 gramme of iodine. *Example.*—20 c.c. $K_2Cr_2O_7$ solution required 16·2 c.c. of sodium thiosulphate; then 16·2 × 5 = 81, which is the number of cubic centimetres of thiosulphate solution equivalent to 1 gramme of iodine. Then 1 c.c. thiosulphate solution = 0·0124 gramme of iodine. Theory for decinorma solution of sodium salt: 1 c.c. = 0·0127 gramme of iodine. A. *Weighin the Sample.*—About 0·15 to 0·18 gramme of oil is to be weighed in glass-stoppered flask holding about 500 to 800 c.c. B. *Absorption o Iodine.*—The oil in the flask is dissolved in 10 c.c. of chloroform After complete solution 30 c.c. of the iodine-mercuric chloride solution is added from a pipette. The chloroform and iodine should give a clear solution; if not, more of the former must be run in for that purpose, and 25 c.c. more iodine if the colour be discharged, as an excess is necessary. After 2 hours the deep brown colour must still be persistent. The flask is now placed in a dark place and allowed to stand, with occasional shaking, for another 2 hours. C. *Titration of the Unabsorbed Iodine.*—300 to 500 c.c. of distilled water is added to the contents of the flask, together with 20 c.c. of the potassium iodide solution. Any iodine which may be noticed upon the stopper of the flask should be washed back into the flask with the potassium iodide solution. Any red precipitate of mercury iodide would indicate an insufficiency of potassium iodide which has to be remedied by adding more. The excess of iodine is now taken up with the standardised sodium thiosulphate solution, which is run in gradually through a burette, with constant shaking, until the yellow colour of the solution has almost disappeared. A few drops of starch paste are then added and the titration continued until the blue colour has entirely disappeared. Towards the end of the reaction the flask should be stoppered and violently shaken, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution in the water. A sufficient quantity of sodium thiosulphate solution should be added to prevent a reappearance of any blue colour in the flask for five minutes. D. *Control Experiments.*—At the time of adding the iodine solution to the oil two blank flasks of the same size and nature as those used for the determination should be employed for conducting the operation described above without the presence of any oil. The difference between the mean of the results obtained by the

IODINE FIGURE, OR RATE OF ABSORPTION OF IODINE PER CENT. OF RAW LINSEED OIL.

Iodine Figure.	Observer.	Iodine Figure.	Observer.
171-175	Lewkowitsch.	173·5-187·7	Thomson & Ballantyne.
170-181	Benedikt.	171-179	Shukoff.
173-195	Ulzer.	176·3	Wijs, by his Iodine Chloride Method.
171-190	Holde.	201·8	

IODINE VALUE OF FATTY ACIDS OF RAW LINSEED OIL.

Iodine Value.	Observer.	Iodine Value.	Observer.
178·5	Williams.	159-185	De Negri and Fabris.
179-182	Lewkowitsch.	179-192	Holde.

IODINE ABSORPTION PER CENT. OF VARIOUS OILS.

Oil.	Minimum.	Maximum.	Average.	Oil.	Minimum.	Maximum.	Average.
Candle-nut	136·3	163·7	150	Walnut .	143	152	150
Beech-nut .	102	112	108-109	Olive . .	79	88	82-83
Cotton-seed	102	111·2	106	Palm .	51	52·4	51·5
Butter .	26	35	33	Castor .	82	85·9	84·5
Coco nut .	8	9·35	8·5	Beef-tallow	35·5	44	39
Cod-liver .	123	166	144-148	Seal . .	96·5	152·4	128
Earth-nut .	87·3	103	94-96	Rape . .	98	104	100-101
Hemp-seed	140·5	166	150	Sesame .	103	112	108-109
Hazel-nut .	83·2	86·9	84·8	Sunflower .	122	134	128
Bone-fat .	46	55	49	Sperm .	81·3	84	82·5
Linseed .	170	195	178	Grape-seed	94	99	96·5
Poppy-seed	134	143·3	138	Whale .	80·9	130	110
				Wood .	149·7	165·7	160

IODINE VALUE AND OTHER "CONSTANTS" OF DIFFERENT BRANDS OF RAW LINSEED OIL. (LEWKOWITSCH.)

Linseed Oil from	Sp. gr. at 15·5° C. (Water at 15·5° C. = 1).	Acid No.	Saponification Value.	Iodine No.	Unsaponifiable Matter, per Cent.	Oxidised Acids, per Cent.
Finest Calcutta linseed, two months old	0·9316	1·3	193·2	170·46	0·6	0·65
Finest Calcutta linseed, three years old, kept throughout that period in an airtight vessel, shielded against light	0·9324	1·3	192·5	174·03	0·7	0·70
Finest Petrograd linseed, three months old	0·9334	1·3	192·2	177·25	1·1	0·88
Finest Petrograd linseed, seven months old	0·9345	1·3	193·1	176·23	0·98	0·56
Baltic linseed, commercial; the seeds contained an admixture of ravison and camelina seeds.	0·9343	1·3	194·3	170·05	1·1	0·73
Finest and purest Baltic linseed; the sample was kept away from light for thirteen years	0·9410	7·2	195·2	175·84	1 1	1·95

IODINE ABSORPTION PER CENT. OF LINSEED OIL AND FATTY ACIDS.

	Iodine Absorption of the Linseed Oils.	Iodine Absorption of the Linseed Oil Fatty Acids.	
		Calculated.	Found.
Fahrion	181·3	190·4	181·4
Holde	171-190	178-200	179-182
Thorner	177-178	181-187	155
Williams	183-188	190-198	178·5

blank experiments and that on the oil corresponds to iodine used, which is brought to per cent. of oil. This number gives iodine figure of the oil. The iodine figure of boiled oil often approaches that of the raw oil, especially, with a rosinate or linoleate drier.

Example :—

Weighed out	155 mgs. linseed oil.
Required for blank experiment . .	47·20 c.c. thiosulphate solution.
Required for actual test . . .	23·85 c.c. ,, ,,
Therefore iodine absorbed . . .	23·35 c.c.

Strength of thiosulphate solution = 0·01175 mg. I. per c.c.

$$\text{Then } \frac{23{\cdot}35 \times 0{\cdot}01175 \times 100}{155} = 177 \text{ per cent.}$$

Origin of Oil.	Iodine Figure.	Density 15° C. / 15° C.	Im-purities, per Cent.	Foreign Seed, per Cent.
DUTCH OILS :—				
(1) Friesland	201·8	0·9352	—	—
”	198·3	0 9346	—	—
”	195·6	0·9333	—	—
”	195·6	0·9337	—	—
”	195·3	0·9339	—	—
(2) Groningen	199·3	—	—	—
”	197·4	—	—	—
(3) Zeeland	193·5	—	—	—
INDIAN :—				
bay	187·5	0·9324	—	—
”	186·0	—	4	—
”	185·7	0·9320	—	—
”	185·6	—	4·44	0·3
”	185·0	—	6·55	0·59
”	184·7	—	4·86	0·42
”	183·9	0 9324	4·04	0·28
”	182·3	0·9313	—	—
(2) Calcutta	182·8	—	4	—
”	182·2	0·9321	4·14	0·94
LA PLATA OIL	182·7	0 9314	3·01	0·17
”	180·0	—	2·17	0·60
”	180·0	—	3·03	0·10
”	179·6	—	—	—
”	178·2	—	—	—
”	177·5	0·9311	—	—
”	176·3	0·9311	1·78	0·00
”	174·7	—	4	—
NORTH AMERICA	188·5	—	—	—
”	182·3	—	2·37	—
”	178·1	—	5·75	—
”	178·1	0·9309	5	—
”	177·8	—	—	—

Origin of Oil.	Iodine Figure.	Density.	Im-purities, per Cent.	Foreign Seed, per Cent.
NORTH RUSSIA :—				
Archangel	192·1	—	—	—
Wiatka	197·4	—	—	—
”	196·4	—	5	—
”	194·0	—	—	—
St. Petersburg	195·0	0·9327	—	—
”	194·2	—	—	—
”	188·5	0·9325	—	—
Reval	198·5	—	8	—
Pernau	198·2	—	10	—
”	196·9	—	5	—
Riga	200·0	—	5	—
”	195·5	—	20	—
”	194·2	—	—	—
Libau	195·5	—	5	—
”	194·6	—	2	—
”	192·4	0·9335	—	—
MID RUSSIA :—				
Samara	189·1	—	—	—
Steppes	188·9	—	2	—
SOUTH RUSSIA :—				—
Azof	182·5	0·9319	—	—
”	182·1	0·9312	—	—
”	181·7	—	—	—
”	181·6	—	—	—
”	179·9	—	—	—
”	179·1	0·9314	—	—
”	178·5	—	4	—
Taganrog	181·7	—	—	—
”	178·3	—	—	—
”	177·9	—	8·66	1·29
”	176·3	0 9305	—	—
Donau	182·1	—	4	—

Wijs' Modification of Determining Iodine Absorption of Oils.—Thirteen grammes of iodine are dissolved in 1 litre of glacial acetic acid on the water-bath, and, after cooling, chlorine is passed through the solution until its titration strength is doubled, a rather sharp alteration in the colour indicating the point. In conducting the analysis from 10 to 20 drops of the oil are carefully weighed into a wide-mouthed stoppered bottle, pure chloroform or carbon tetrachloride is added, and when oil is dissolved 25 c.c. of the Wijs' solution. After standing for 15 minutes potassium iodide solution is further added, and the volume made up to 150 c.c. with water. It is then titrated with thiosulphate in the usual manner, including blank experiment. The Wijs' method agrees somewhat closely with the Hübl, but the former gives rather higher results. Harvey found with rape oil (Hübl's method) 101·6 and 104·9. Cod oil seems to give as much as 7 or 8 per cent. higher by the Wijs' method than by Hübl's. The advantages of the Wijs' process are rapidity (earth-nut absorbs 98·9 per cent. of its full quantity in one minute), stability of solution, and quick and accurate results. The previous table gives Wijs' results with raw linseed oils of different origin.

Wijs tried to show that the density of the oil and the iodine number were correlated as shown by above table.

McIlhiny's Bromine Absorption Method.—About 0·2 gramme of the linseed oil to be tested is placed in a glass-stoppered bottle, 10 c.c. of carbon tetrachloride added to dissolve the oil, and then 20 c.c. of third normal bromine in carbon tetrachloride run in from a pipette. Another pipetteful is run into another similar bottle. It is convenient, but not absolutely necessary, that both bottles should now be cooled by immersing them in cracked ice. This causes the formation of a partial vacuum in the bottle. The bromine need not be allowed to react with the oil for more than a few minutes, as the reaction between them is nearly instantaneous. Twenty-five c.c. of a neutral 10 per cent. solution of potassium iodide is introduced into each bottle by slipping a piece of rubber tubing of suitable size over the lip of the bottle, pouring the iodine solution into the well thus formed, and shifting the stopper slightly so as to allow the solution to be sucked into the bottle, or, if the bottle has not been cooled, to cause the air as it escapes from the interior to be washed by bubbling through the potassium iodide solution. This prevents the loss of any bromine or hydrobromic acid. The iodide solution introduced, the bottle is shaken, and set in ice for a couple of minutes more, so that there may be no loss when the stopper is opened, due to slight pressure inside the bottle. The solution reaction causes heat and pressure. The free iodine is now titrated with tenth-normal sodium thiosulphate, using as little starch as possible as indicator. At the end of this titration 5 c.c. of a neutral 20 per cent. solution of potassium iodide and a little more starch solution are added, the iodine liberated, on account of the hydrobromic acid produced in the original action of bromine on the oil, and titrated with thiosulphate. From the figures so obtained, the total percentage of bromine which has disappeared is calculated, and the percentage of bromine found as hydrobromic acid, called the "bromine substitution figure," is also calculated, while from these two the "bromine addition figure" is obtained by subtracting twice the bromine substitution figure from the total bromine absorption—

Iodine Number.	Number of Samples.	Density $\frac{15}{15^{\circ}}$
> 200	1	0·9352
195·1 to 200	4	0·9339
190·1 ,, 195	4	0·9329
185·1 ,, 190	4	0·9322
180·1 ,, 185	6	0·9317
< 180·1	5	0·9310

TABLE SHOWING THE GREAT VARIATIONS IN THE IODINE NUMBER OF DIFFERENT SAMPLES OF LINSEED ACCORDING TO DIFFERENT OBSERVERS AND AS DETERMINED BY DIFFERENT METHODS.

Authority.	Iodine Numbers, and Process Used	Authority.	Iodine Numbers, and Process Used.
American Committee	183·9-186·4 Hanus.	Marcusson .	174·8 H. or H. W. 192·5 Wijs.
Fahrion .	171-183 H. or H. W.	Mastbaum .	178-183 H. or H. W.
Filsinger .	178·4-185·3 ,,	Niegemann .	169·4-180·5 ,,
Gill and Lamb .	178-180 ,,	Shukoff .	171-179 ,,
Holde . .	171-189 ,,	Sgollema .	164·0-185 ,, 177·6-198·1 Wijs.
,, . .	171 190 ,,		
Hunt . .	174·8 ,,	Thomson and Ballantyne	173·5-187·7 H. or H. W.
,, . .	177·3 Wijs.		
,, . .	174·5 Hanus.	Thompson and Dunlop	185·5-205·4 Wijs.
Kelel and Anlusch .	181-187 H. or H. W.	De Vries .	183·6-204·6 ,,
Kitt . .	174·3-175·3 ,,	Wijs . .	180·9 H. or H. W. 182·2 Wijs.
,, . .	171·9-177·7 Hanus.	,, . .	177·6 H. or H. W.
Lettenmayer	183·8-193·3 H. or H. W.	,, . .	178·1 Wijs.
Lewkowitsch	170·5-177·3 ,,	,, . .	182·2-201·8 Wijs.
,,	173-193 Wijs.	Williams .	183-188 Wijs.

$$C_nH_{2n}O_2 + Br_2 = C_nH_{2n-1}O_2Br + HBr.$$

Fatty acid. Bromosubstitution product.

is present. If the bromine substitution figure is normal the absence If an oil contains rosin, rosin oil, or mineral oil, the fact is brought out, and an indication given by the figures so obtained as to which one of more than a very small quantity of turpentine, benzine, rosin, or rosin oil is assured. The process can be carried out in the time necessary for weighing and titrations, as the standard solution, unlike the Hübl solution, does not deteriorate on keeping if tightly closed, so that it is always ready for immediate use, and there is no waiting for some hours for the reagents to act upon the oil, as in the Hübl process, the reaction taking place immediately. The bromine *addition* figure of linseed oil lies ordinarily between 100 and 110. Age lowers the halogen figures of linseed oil. A low "addition figure" may also be caused by rosin, rosin oil, benzine or mineral oils, which have figures usually below 15; by the presence of some other seed oil, the commonest of this class being corn and cotton-seed oils, having figures in the neighbourhood of 73 and 63 respectively; or by the oil, in case it is a boiled oil, having been boiled in the old-fashioned way at a high temperature. If the "addition figure" is very much higher than 110, it will be found that the oil contains turpentine, as all other foreign materials added have lower figures than linseed oil. The "bromine substitution figure" of genuine linseed oil is about 3. A much higher figure would point to turpentine, rosin, or rosin oil, which give figures from 20 to 90; to the presence of some petroleum product, as benzine, having a figure in the neighbourhood of 15, or a heavier petroleum oil, which may have as low a figure as linseed, or may be much higher; or to the presence of mineral acid in the oil, which may be allowed for by a separate determination of its amount, as described under the determination of the "acid figure".

Both the Hübl and the "bromine addition figures" are practically the same for boiled oil as now made as for raw oil. Boiled oil made by the old process at a high temperature distinctly lower figures on account of the effects of the great heat upon the oil. The amount of bromine equivalent to the iodine absorbed as expressed by the Hübl figure has been calculated, and by dividing this result by the "bromine addition figure," a figure obtained for each oil which is intended to express, by the amount it exceeds 1000, the amount of substitution of iodine which has gone on in the Hübl iodine absorption. For example, if the figure obtained for an oil by the calculation described is found to be 1·075, it indicates that the Hübl figure is in that case 7·5 per cent. higher than the true iodine figure, which should express the iodine absorption by addition. The "bromine addition figure," is not sensibly affected by the time the oil is allowed to remain in contact with bromine, but the "bromine substitution figure" probably is. The difference between five minutes' and thirty minutes' contact, however, does not appear to be marked, unless the substitution figure is very high, as pure rosin or turpentine.

In carrying out either the Hübl or the bromine process upon oils it is necessary that an excess of iodine or bromine should be used amounting to as much as the oil absorbs. Many iodine figures on record are too low because this precaution was not attended to. More information is to be obtained as to the character of a sample of linseed oil by determining the bromine figures than by any other single test. In the case of an oil of unknown character, it would in most cases be advisable first to apply this test to it (McIlhiny).

McIlhiny found for a raw linseed oil the iodine value of 184·2 by Hübl's method and a total bromine absorption of 116·1, which number agreed closely with that calculated from the iodine number 116·5.

McIlhiny's method involves the use of ice for cooling purposes and that is a drawback which has militated against its adoption. W. Vaubel claims to have given the method a more handy form. The oil is dissolved in chloroform or carbon disulphide and agitated with an aqueous solution of potassium perbromate, $KBrO_4$ and KBr. Instead of thiosulphate sodium sulphite is used to estimate the excess of bromine. If the bromate solution is not used in excess but the acetic acid solution of the fat titrated direct by HCl and KBr, a portion of the double bond remains intact. Linseed oil gave a primary bromine number of 75·5 to 80 and a secondary bromine number of 107·7, from which the iodine absorption number of 170·7 is calculated.

The Percentage of Insoluble Bromine Derivatives. The Hexabromide Number.

This determination was proposed by Hehner and Mitchell ("Analyst," Dec., 1898, vol. xxiii., p. 310). It depends upon the fact that linseed oil, when dissolved in ether and treated with bromine, gives direct bromination compounds of glycerides and bromine which are insoluble in the ether, while oil containing glycerides of oleic acid only, and even semi-drying oils like cotton-seed and corn oils, give soluble compounds. 1 to 2 grammes of the oil are dissolved in 40 c.c. ether, and acetic acid added in a closed flask, cooled to 5° C., and bromine added drop by drop until the red coloration becomes permanent. After standing for 3 hours the insoluble bromine derivative is filtered through asbestos, washed with 5 c.c. of acetic acid alcohol and ether, and dried on the water-bath until of constant weight. The fresh hexabromide number of linseed oil varies generally between 20 and 26, but higher results have been obtained :—

Hehner and Mitchell	23·86 to 25·8
Walker and Warburton	23·1 ,, 28·52
Lewkowitsch, 1864	24·17
,, 1904	37·72

Hehner and Mitchell obtain the following percentages of insoluble bromine compounds from different oils:—

	Per Cent.
Linseed oil	23·86 to 25·8
Poppy oil	0·0
Corn oil	0·0
Cotton-seed oil	0·0
Olive oil	0·0
Almond oil	0·0
Rape-seed oil	0·0
Whale oil	25·0
Cod oil	34·5
Cod-liver oil	42·9
Shark oil	22·0

The process, which seems to be a valuable one, detecting adulterations of linseed oil with other seed oils, has been satisfactorily reported on by McIlhiny. Two samples of raw linseed, six samples of boiled linseed, two of corn, and one of cotton-seed oil, tested by him, gave results agreeing substantially with those of Hehner and Mitchell. Two samples of mineral oil, one light and one heavy, one sample of rosin oil, and one sample of turpentine failed to give any precipitate of insoluble bromine derivatives.

Maumené's Thermal Test.—1. The sulphuric acid to be used in this experiment should be pure, of specific gravity 1·845, and should be kept in a well-stoppered and capped bottle. The stopper should not be left out a moment longer than that required to extract the necessary quantity. Have the acid in a bottle 6 inches high, with a thermometer inside.

2. Counterbalance a glass tube, on foot, standing heat (about 1½ inches in diameter and 7 ounces capacity), and weigh in accurately 50 grammes of the oil.

3. Immerse both the sulphuric acid and the tube containing the oil in water contained in a tin vessel 5 inches deep, 2 quarts capacity, and apply heat. As soon as both the acid and the oil are at a temperature of 20° C., draw out 10 c.c. of the acid with a pipette and let it flow gradually at the rate of 1 c.c. every 5 seconds into the oil, without touching the sides, stirring very energetically all the time with the thermometer. After all the acid is in continue to stir exactly for half a minute, then move the thermometer more slowly, noting the exact degree at which it ceases to rise.

A pure sample of oil should be tested in the same manner precisely, immediately before the suspected article. No two persons, unless actually working side by side, will ever get absolutely identical figures, and rarely then. So delicate is the rise of temperature that the same operator must needs be careful to obtain constant figures on repeating the experiment on the same oil. It is customary to record results expressing the nett rise of temperature thus: Let total temperature rise be 130° C., initial temperature 20° C. Then 130° C.

- 20° C. = 110° C., which would be about the Maumené number for genuine raw linseed oil.

In the case of linseed oil and fish oils the reaction is energetic, abundant fumes being given off, whilst the mixture assumes a gluey consistence; thorough mixing of the acid and oil is a matter of great difficulty. Moreover, it is not at all easy to obtain satisfactory readings of the thermometer, the more so as the latter has to be used to stir the oil. It is therefore advisable to mix linseed, etc., oils in known proportion with an oil on which sulphuric acid has no great action, such as petroleum lubricating oils.

Knowing the heat given out by mixing the mineral oil alone with sulphuric acid, it is easy to calculate how far its admixture with linseed oil has affected the latter.

MAUMENÉ'S TEST, RESULTS WITH TYPICAL OILS.

Oil.	Maumené.	Baynes.	Archbutt.	Allen.	De Negri and Fabris.
Linseed	103	104-124	—	104-111	122-126
Hemp-seed . . .	98	—	—	—	95-99
Walnut . . .	101	—	—	—	96
Poppy-seed . . .	74	—	86-88	—	87-88·5
Niger-seed . . .	—	82	—	81	—
Sunflower . . .	—	—	—	—	72-75
Soja-bean . . .	—	—	—	—	117
Cotton-seed (crude) .	—	84	70	67-69	—
,, (refined)	—	77	75-76	74-75	—
Olive	42	40	41-45	41-43	32-37
Dolphin . . .	—	—	42	41-47	—
Menhaden . . .	—	—	123-128	126	—
Cod liver . . .	102-103	116	—	113	—
Whale (Arctic) . .	—	—	—	91	—
,, (Antarctic) .	—	—	92	—	—
Seal	—	—	—	92	—

Specific Temperature Reaction (Thomson and Ballantyne).—The rise of temperature obtained by mixing 50 grammes of oil with 10 c.c. of sulphuric acid, divided by the rise of temperature produced by mixing 50 grammes of water with 10 c.c. of the same sulphuric acid, in the same vessel and under identical conditions, gives a quotient termed the specific temperature reaction.

Origin of Oil.	Authority.	Specific Temperature Reaction.	Origin of Oil.	Authority.	Specific Temperature Reaction.
Baltic . .	Thomson and Ballantyne	349	River Plate .	Thomson and Ballantyne	320
East Indian .	,,	320	—	Jenkins	313

Thermal Values of Fats and Oils.—The Maumené test, i.e. the heat generated by acting upon oils with strong sulphuric acid. Marsden and Dover describe the apparatus used by them and give the heat of dilution of the sulphuric acid employed by them and the method of standardising the apparatus, which is essentially a Dewar's tube used as a calorimeter. The rise in temperature for various oils are given in a table calculated in calories per gramme of oil, using acid containing 95·10 per cent. of H_2SO_4. The effect of different strengths of sulphuric acid was also investigated, and a table of the specific heats of oils, fats, and waxes is also given.

Elaidin Test.—This is a very simple test for differentiating between drying and non-drying oils, requiring no costly apparatus when applied according to Poutet's original instructions. The proper way to apply the test is as follows: A. *Apparatus required*—(1) Supply of 2-ounce conical test glasses on feet. (2) A swan-neck minim measure. (3) Mercury ¼ lb. in narrow-mouthed stoppered bottle. (4) Glass rods rounded at one end and dubbed out at the other. (5) Glass flask, 30 ounces. B. *Preparation of the test solution*—Weigh out in any suitable glass vessel, such as a small beaker, 60 grammes of metallic mercury, run it into the capacious flask; place the latter in a vessel of water in a stink-closet, or in a good draught; then add carefully and gradually, a little at a time, 75 grammes of nitric acid, specific gravity 1·37 (74° Twaddell). Keep the flask well immersed in the water to condense the fumes, which are partially retained by the solution and constitute its acting principle. Transfer to a well-stoppered bottle, and label it olive oil test with date, as it does not keep so very long.

C. Harrison (Department Oil Colours, the Borough Polytechnic Institute) obtains excellent results by adding mercury and nitric acid direct to a well-fitting stoppered bottle. After addition of the materials the stopper is tightly fixed, quickly tied over, and immersed with occasional shaking in ice-cold water until reaction has ceased, when the solution is ready for use. Working this way a characteristic green solution is obtained, and if kept closely stoppered will be preserved for upwards of two years or more.

Process.—Pour into a 1-ounce conical test glass on foot 10 minims of the above solution. From a separate minim measure run in 100 minims of oil on to the top of the mercury solution. Thoroughly incorporate the mercury solution and the oil by stirring continuously with a small glass rod, dubbed out at the end by having been heated till viscous in a bunsen or blowpipe flame, and then pressing it against a slab of slate, stone, etc. Repeat the test on a known sample of pure olive oil, and with olive oil adulterated, respectively, with 5 per cent., 10 per cent., 15 per cent., 20 per cent., 25 per cent., and so on with any drying oil. The test is best performed at five o'clock at night, and the set of samples set aside with their respective rods resting in the test glasses on feet until next morning at nine. Treated olive oil, gives a canary-coloured hard mass which can be lifted completely out of the test glass by the glass rod absolutely intact, and while still adhering thereto if it be struck against the test glass it emits a metallic resonant sound or musical note. Most writers refer only to the time which oils take to solidify under the action of this reagent. The author prefers, as the result of prolonged expreience in the testing of olive oil, to take the ultimate hardness and colour after a reasonable time, say, 5 p.m. to 9 a.m., as the standard to go by; and the results have never been called in question. It would be well if innovating analysts would test the original process thoroughly before modifying it for the mere sake of the vainglory of adding one more useless modification to numerous others. Poutet's process was perfect before he enunciated it. The innovators have only brought an excellent method into disrepute. They have never taken the trouble to test the original method but have acted on the utterly unsound principle that because a method is an old method its results must be false, and their own methods with a trace of novelty are perforce the only true ones; but therein lies degeneration.

CHAPTER VIII.

THE PHYSICAL PROPERTIES OF LINSEED OIL.

THE DETECTION OF ADULTERATION IN LINSEED AND OTHER DRYING OILS BY ORGANOLEPTIC AND PHYSICAL METHODS.

A. Organoleptic properties of linseed oil, (1) smell, (2) taste, (3) colour.

1. *Assessing the Value of a Sample of Raw and Boiled Linseed Oil by Smell.*—So characteristic is the smell of raw linseed oil that it is almost impossible to add any oil to linseed oil which has got a pronounced odour without that odour being almost as pronounced in the raw oil to which it is added as it is in the original adulterant. Rosin oil and fish oils make themselves felt in linseed oil by their characteristic and powerful odours. The trade is told that linseed oil itself develops a fish oil smell as it oxidises. But it may safely be said it does not do so under normal conditions. Under abnormal conditions it may develop a sort of putrefactive fermentation as when scrim is stored in badly corked bottles. Scrim is an unfinished reaction, and no one in his senses would apply an unfinished product to perform by itself alone the functions of a finished product. He would be a still more foolish person that would make any deductions whatever from this unfinished unstable product and apply them to thoroughly dried paint films. What have thoroughly dried paint films to do with half-dried oil skins? There is no analogy between scrim and the linoxyn of a real dry paint film. Fish oil is perhaps not so readily revealed by its smell in boiled oil, but it manifests itsel even then when energetically rubbed between the palms of the hands as if one were making a lather, and then applied to the nostrils The characteristic smell of burning rosin is developed when the oi is burned, if it should contain either rosin or rosin oil. The smell of the pure genuine oil is very characteristic, especially when newly pressed; it then has a bland, mucilaginous, appetising odour, forms the very best and most palatable and most wholesome of edible oils but this odour gives place as the oil ages to a somewhat rank, but no unpleasant, though still characteristic smell. The newly pressed oi should not give off the smell of cooked turnips which have been over-heated in the operation. That is a sign that the oil has been made from seed containing rape, or other cruciferous oils, and that i

has been extracted at too great a steam heat. The nose is a very useful factor in the testing of oils, and no opportunity should be lost in training and exercising it in its duties in this respect. But one must not be led away even by a smell into the fields of imagination; one must not imagine himself in Dante's Inferno every time one smells sulphur. None the less the man who handles linseed oil or paint should know the smell of crude gasolene when present in an oil-can or in an anti-fouling composition or other quick-drying paint. But motor-cars have popularised gasolene. The stench of the former article was its danger signal.

An abnormal uncommon smell in linseed oil is generally due to fish oil and rosin oil, etc., also to some volatile oil or another. When water is distilled over linseed oil, or when linseed oil is treated with a current of steam, it should yield no other distillate than condensed water; a volatile distillate would point to spirits of turpentine or petroleum spirit.

2. *Taste.*—The taste of linseed oil is also as characteristic as its smell; when new it is bland and pleasant; old oil is slightly acrid. Fish oils can hardly be detected in linseed oil by their taste unless present in large proportion but the most minute trace of rosin oil can most easily be detected. When a linseed oil containing rosin oil first impinges on the palate nothing very much amiss is discovered at first, and the operator thinks, as far as taste is concerned, the oil is all right, and perhaps if uninitiated goes away satisfied to perform some other test on the oil, but by-and-by a bitter, biting, acrid, nauseous taste makes itself felt on the back part of the palate, which, in pronounced cases, makes one shudder and expectorate to get quit of it. But it remains persistent for some considerable time. There is no necessity to recall the taste of rosin oil, one remembers it all one's life.

3. *Assessing the Commercial Quality of any Given Sample of Raw Linseed Oil by its Colour.*—The colour of *raw linseed oil* is usually a brownish-yellow, while refined linseed oils are almost colourless. Baltic linseed oil is a dark olive-green in bulk and not at all a pleasant-looking liquid. A blue or green fluorescence exhibited when the oil is looked at on a black background with the back to the light is a sure sign of adulteration with either mineral or rosin oil. This bloom may be somewhat removed from the rosin oil by the addition of ½ lb. to 1 lb. of di-nitro-naphthalin to every 10 gallons of rosin oil, but the method is too costly; besides the fluorescence has a tendency to return. Moreover, the nitro-naphthalin renders the oil acid, and, besides, it throws the rosin or mineral oil several shades back in darkness of colour. Again, the nitro-naphthalin leaves a residuum or organic nucleus in the oil which readily lends itself to detectio (see vol. iii.).

Assessing the Quality of any Given Sample of Boiled Linseed O by its Colour.—This may vary from the pale colour of the raw oil itse when soluble driers are used, e.g. manganese linoleate aided by blowing the oil, to port wine or even porter colour, the latter colour being characteristic of oils from which the oxide drier has not had time to settle out. Fluorescence or bloom should be carefully looked for by spotting a drop of the oil on black paper, or on the black cover of a note-book, and turning the back to the light, lowering the paper to the knees, and gradually raising and lowering it at several inclinations. If any rosin oil or mineral oil be present it generally shows itself by the bloom manifested under these circumstances. But the bloom is not so readily seen in boiled as in raw oil, especially when the rosin oil has been boiled along with the linseed. When the rosin oil is boiled along with the linseed, so long as not more than 2 or 3 per cent. of rosin oil is used, the practice is not quite so bad as at first sight might appear; the acidity of the rosin oil is corrected by the litharge, and the rosin acids are converted into rosinate of lead, and thus assist in stimulating the drying propensities of the oil, and the profit on this small addition pays for the cost of boiling. The painter does not care to pay much higher for his boiled than he does for his raw oil, and to this extent he shows himself unreasonable. When the oil is full of flaky matter, and even after filtration continues to deposit foots, it points to common cotton-seed oil having been boiled with the oil. Its stearine separates out *ad infinitum*.

The Natural Fluorescence of Printing Ink Vehicles.—Burnt oil made from pure raw linseed oil must not be mistaken for the adventitious fluorescence due to rosin or mineral oils. It is due to a pyroligneous product produced during the burning of the oil. The colour of linseed oil from a bleaching point of view is dealt with elsewhere.

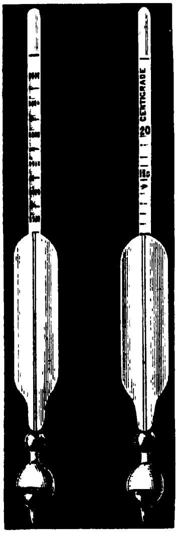

FIG. 44.—Thermohydrometers for oil.

Physical Properties of Linseed Oil.—(1) Specific gravity; (2) viscosity; (3) index of refraction; (4) optical deviation of light polarimetry; (5) m.p. of oil; (6) m.p. of fatty acids; (7) solidification-point of oil; (8) solidification-point of fatty acids.

Specific Gravity.—The specific gravity of linseed oil at any given temperature is its weight compared with the weight of an equal bulk of water at the same temperature taken as unity. Sometimes, however, the density at 100° C. (212° F.) is referred to water at 15° C., or 60° F. (15·5° C.), and so on. The reason of this is that the specific gravity bottle which is used to take the density of the oil is graduated at, say, 60° F. Moreover, the difficulties in graduating a specific gravity bottle

212° F. are sufficiently obvious. The specific gravity bottle may be had graduated to hold 1000 grains at 60° F. or 50 grammes or 100 grammes. When the bottle and stopper are tared in the case of the 1000 grains bottle, the number of grains added to restore equilibrium gives directly the specific gravity of the oil, but in the case of the 50 grammes or 100 grammes the exact weight added to restore equilibrium has to be multiplied by 20 or by 10 respectively. For all practical purposes the density of linseed is taken with sufficient accuracy by the hydrometer. The most useful hydrometer for linseed oil testing is graduated from ·900 to ·950. The oil refiner and boiler could not invest in two more serviceable instruments. Life is too short for taking the specific gravity of linseed oil by specific gravity bottles or Westphal balances. It is only wanted to the third decimal point, and that is given correctly by any accurate hydrometer. It will be seen that no two observers agree in regard to the gravity of linseed oil at any given temperature. Possibly some of these variations are due to experimental errors, but as a matter of fact it would be very difficult to get two samples of oils representing different bulks to coincide exactly in density, and not only in density,

TABLE OF FORMULÆ FOR CONVERTING DEGREES OR INDICATIONS OF VARIOUS HYDROMETERS INTO ACTUAL GRAVITY.

Hydrometer	Temperature of Graduation.			Fluids Heavier than Water.	Fluids Lighter than Water.
	°C	°F.	R.		
Ball. . .	17·5	—	—	$S = \frac{200}{200 - n}$	$S = \frac{200}{200 + n}$
Baumé . .	15·625	60·125	12·5	$S = \frac{144}{144 - n}$	$S = \frac{144}{144 + n}$
Baumé . .	15	59	—	$S = \frac{144{\cdot}3}{144{\cdot}3 - n}$	$S = \frac{144{\cdot}3}{144{\cdot}3 + n}$
Baumé . .	17·5	63·5	—	$S = \frac{146{\cdot}78}{146{\cdot}78 - n}$	$S = \frac{146{\cdot}78}{146{\cdot}78 + n}$
Beck . .	15·625	60·12	12·5	$S = \frac{170}{170 - n}$	$S = \frac{170}{170 + n}$
Brix . . .	15·625	60·125	12·5	$S = \frac{400}{400 - n}$	$S = \frac{400}{400 + n}$
Cartier . .	15·625	60·125	12·5	$S = \frac{136{\cdot}8}{126{\cdot}1 - n}$	$S = \frac{136{\cdot}8}{126{\cdot}1 + n}$
Fischer . .	15·625	60·125	12·5	$S = \frac{400}{400 - n}$	$S = \frac{400}{400 + n}$
Gay-Lussac .	4	39·2	—	$S = \frac{100}{n}$	$S = \frac{100}{n}$
E. C. Greiner .	15·625	60·125	12·5	$S = \frac{400}{400 - n}$	$S = \frac{400}{400 + n}$
Stoppani . .	15·625	60·125	12·5	$S = \frac{166}{166 - n}$	$S = \frac{166}{166 + n}$
Twaddell . .	—	60	—	$S = 0{\cdot}005 \times n + 1{\cdot}000$	—

but in other particulars, and it may be advisable to discuss here once for all, the reasons for this continual variation. The density of linseed oil, like all its other so-called chemical and physical "constants" (*sic*), varies (1) with the general purity and with the pedigree of the seed from which the plant which produced it sprung; (2) with the soil on which the plant producing the seed (which when crushed yielded the oil) grew; (3) with the climate in which that soil was located; (4) with the manure applied to the crop; (5) with the time of sowing; (6) with the previous rotation of crops; (7) with the season whether wet or dry; (8) with the after cultivation; (9) with the time of harvesting, i.e. whether the seed was allowed to ripen too little or too much, i.e. whether or not the exact moment was seized for harvesting the crop, when the oil in the seed was in that state of maturity in which, after rational harvesting of the flax, threshing and storage, and winnowing of the seed and expression therefrom of the oil, the latter excels in all those good qualities for which linseed oil is so justly and so highly esteemed. Examples of influences which affect the linseed crop adversely need not be multiplied. Independently therefore of impure seed and adulteration of the oil, whether by intentionally crushing it with a greater or less amount of seed which is not linseed, or after expression by the addition of an oil previously expressed from seed which is not linseed, or by the addition of marine animal oils (fish oil, whale oil, etc.), mineral oils or rosin oil, the density of genuine linseed oil, like every other so-called chemical and physical constant, varies within rather wide limits. It is a very difficult matter indeed to convince the uninitiated that the properties of genuine linseed oil are not like the law of the Medes and Persians, "which altereth not". But having gone into the reasons why raw linseed oil varies in composition and properties, it will only be necessary to refer to the matter again when it is especially important to do so. Presuming, however, that we are dealing with a genuine oil, the density should never go below 0·931 nor above 0·934 in the case of raw linseed oil. Books and trade journals give higher densities, but the normal oil is not to be met with on the market with a higher density than 0·934; even 0·933 is rare. The linseed-oil consumer is to a great extent indebted to the farmer for the purity of the oil supplied to him. The crusher must needs sell his oilcake, and as, e.g. rapeseed can be detected under the microscope and also by chemical means in the linseed cake, the crusher cannot very well crush a certain amount of non-drying oil with his linseed should it yield an oil of very high gravity. He can, of course, sophisticate it afterwards, but some crushers innocently imagine that if they crush the two seeds together, and thus treat the oil exactly alike, the fraud will escape detection. So it may if the linseed oil from that particular batch of seed be of itself of high gravity and yield high tests generally. The rape-seed oil crusher has mountains of unsaleable rape which he ould if he could sell in the form of linseed cake. But then the usher would be in hot water with the farmers and the agricultural cieties to which they belong; his oilcake would get a bad name, and the end the crusher would only prove once more that honesty is e best policy. The farmer is the paint-grinder and varnish-maker's st friend. His chemical and microscopical control of the linseed lcake market is perfection. This control has long reacted on the urity of linseed oil without the users ever giving it a thought.

Oils of Similar Gravity to Linseed Oil.—The only oils approachng linseed oil in gravity are Lallemantia oil and certain fish or arine animal oils, which can be detected by methods given in the equel. The specific gravity of wood oil is much higher than linseed oil, viz. 0·940.

Oils of Different Gravity to Linseed Oil.—All other vegetable drying and non-drying oils are specifically lighter than linseed oil, with the exception of wood oil, castor oil, croton oil, rosin oil, the hydrocarbide oil produced by the destructive distillation of rosin. When linseed oil is dear there might be a tendency to adulterate it with lower grade castor oil. The greater density, unless manipulated to meet the case by the addition, say, of rape oil, would at once indicate the sophistication, but here comes in the bad effect of the high maximum densities given in books. Supposing 10 per cent. by volume of castor oil 0·960 gravity were added to a linseed oil of 0·931 gravity,

We get 9 × 0·931 = 8·379
„ „ 1 × 0·960 = ·960
10)9·339
0·9339

Now, as far as specific gravity is concerned, no one can go into a court of law—in face of the traditionary matter in regard to the specific gravity of linseed oil given in books—and swear that the above sample ot genuine linseed oil. But happily every particle of the castor can be separated by alcohol and weighed. So the sophisticator to bear in mind that his oil must not satisfy one test alone; it ust satisfy at least a score of tests. Rosin oil can be separated out m linseed oil almost as easily as castor oil; when the soft soap, ade from a linseed oil containing rosin oil, is dissolved in water and shaken up with ether, the latter extracts all the rosin oil and floats to the top of the soap solution from which it is decanted, the ether distilled and the rosin oil weighed as already described

SPECIFIC GRAVITY OF RAW LINSEED OIL FROM VARIOUS SOURC

Observer.	°C.		Density.	Origin.	No. of Sample.	
1. Allen . .	15		0·932-0·937	—	—	—
,, . .	99		0·8809	—	—	—
2. De Negris and Fabris .	15		0·9342	—	—	—
3. Filsinger .	17·5		0·9305	—	—	—
,, .	·15 15	15·5 15·5	0·9329	Germany	1	Edible oil
,, .	,,	,,	0·9329	India	1	For oil boiling
,, .	,,	,,	0·9321-0·9326	—	2	English crushe
4. Gill and Lamb	,,	,,	0·931-0·934	U.S.A.	4	—
4a. Henriques .	,,		0·9315-0·937	—	—	—
5. Holde . .	20		0·9275-0·935	-	—	—
6. Lewkowitsch	15·5		0·9316-0·9345	-	—	—
,,	,,		0·9316	Calcutta	1	—
,,	,,		0·9334	Petrograd	1	—
,,	,,		0·9348	Baltic Provinces	1	- -
7. McIlhiny .	—		0·931-0·937	U.S.A.	—	—
8. Niegemann .	—		0·9290-0·9325	Russia	5	—
,,	—		0·9290-0·9330	La Plata	9	—
,, .	—		0·9305	India	1	—
9. Laussure .	12		0·933	—	.	—
,, .	25		0·930	—	—	—
,, .	50		0·921	—	—	—
,, .	94		0·881	—	—	—
10. Scheibler .	15		0·9347	—	—	—
11. Shukoff .	—		0·935-0·936	—	—	—
12. Souchere .	—		0·9325	—	—	—
13. Stillwell .	18		0·9299	—	—	—
,, .	,,		0·9411	—	—	—
14. Thaysen .	—		0·9300-0·9330	—	5	—
15. Thomson and Ballantyne .	15		0·9315-0·9345	—	—	—
16. Tomarchia .	—		0·9320	Italy	1	—
,, .	—		0·9358	Bombay	1	—
,, .	—		0·9325	Morocco	1	—
,, .	—		0·9360	Marmora	1	—
,, .	—		0·9330	La Plata	1	—
,, .	—		0·9372	Russia	1	—
17. Utz . .	—		0·9297-0·937	—	22	German crus
18. U.S.A. . .	—		0·9329-0·9345	U.S.A.	4	—

[1] Add or subtract 0·004 for every 10° F. above or below 60° F.

[2] Water at 15·5° C. = 1.

Density of fatty acids of linseed oil—

at 15·5° C. = 0·9233 (Allen).

at 99° C. (water at 15° C. = 1) = 0·8612 (Allen).

at 100° C. (water at 100° C. = 1) = 0·8925 (Archbutt).

The accompanying graph (see opposite page), due to Laurent, does away with all calculation and immediately gives the density of an oil at any temperature.

Explanation.—The following explains the principle of this table which anyone may construct for himself on the same lines: To the left are the densities. On the top and horizontally are the tempera- lying between 10° and 30° C. (50° to 86° F.); the oblique lines the names of certain oils are expansion lines; the transversal

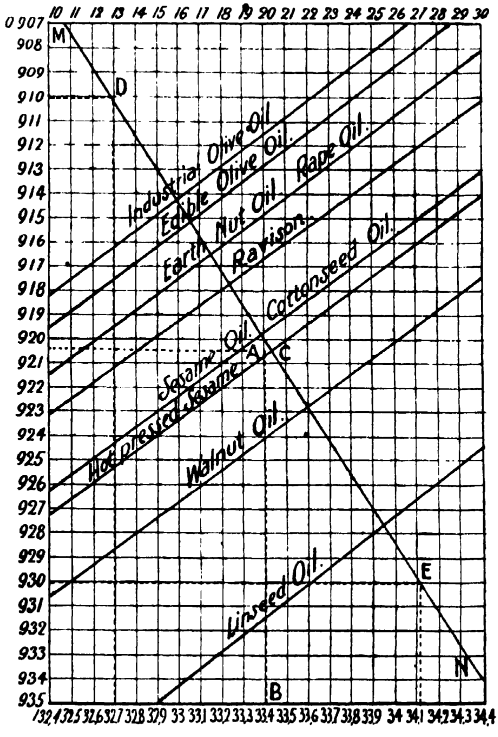

FIG. 45.—Graphical representation, after Laurent, of the alteration in gravity which oils undergo under the action of heat (expansion), lower gravity, and cold (contraction). The top horizontal figures are degrees centigrade. The vertical figures are specific gravities at the temperature at which the horizontal line corresponding to the gravity cuts the diagonal line.

line MN is the line corresponding to the weight of the flask full of oil which is determined thus. In the example given above the density of 0·9205 has been found; this density is sought for to the left of the graph which lies between 0·920 and 0·921. The dotted line AB is followed, and at the point B the weight of the flagon full of oil is 133·46. But so as to make each decigramme correspond to a vertical line, it is convenient to write 133·40 instead of 133·46, and alongside A the point C is marked corresponding to the fraction 0·46, as the point through which the line MN must pass. Thus there is inscribed to the left of 133·4, 133·5, 133·6, etc., to the last vertical line, and to the left, 133·3, 133·2, all to the first vertical line. Two other points of passage are determined corresponding to two densities, one of which is lower than 0·9205, as 0·910, and the other higher, as 0·930; for example, by calculating what are the weights of the flask full of oil corresponding to these densities, the density 0·910 being the quotient and the weight of water at 4·1° C. – 70·65 the divisor; these two numbers are multiplied the one by the other, and we get the dividend 64·29, the net weight of the oil to which, when the tare of the flask, 68·43, is added, we get the weight of the flask full of oil = 132·72. Starting from this weight inscribed at the bottom of the table and ascending to the density 0·910, the point is marked. Operating in the same way for the density 0·930 the point E is marked. The line MN is then drawn through the points C, D, E. This graph being so constructed, suppose the gross weight of the flask full of the oil to be tested is 133·20 at a temperature of 24° C. without any other calculation, we have only to find this weight inscribed at the bottom of the table, ascend the corresponding vertical line until it meets the line MN, then follow the horizontal line until it meets the vertical line corresponding to the temperature of 24°, that is on the line for cotton-seed oil and sesame oil, the density which is 0·917, is read off to the left. If it be desired to bring this density to 15° C., the expansion line marked Sesame is followed to the vertical line corresponding to 15° C., the density is read off to the left as 0·923. That density is expressed with reference to water at + 4·1°. It suffices to multiply by the factor 1,000,841 to express the density with reference to water at 15° C.

Determination of the Specific Gravity by Sprengel's Tube.—When the specific gravity has to be determined in a very precise manner, specific gravity bottle and picnometers are used, particularly Sprengel's tube. Sprengel's tube is a U tube, the two vertical branches of which are united underneath by a narrow curved tube, and terminated in the upper part by two narrow tubes bent to a right angle, the ends of which are closed by two glass stoppers. Their diameter is unequal; that carrying the mark is about twice as wide as the other one which is about 0·25 mm. in diameter. It is suspended from the beam of a sensitive balance by a wire, preferably platinum, so as to determine its weight before and after filling. The tube is filled by immersing the tube carrying the mark in the oil and aspirating from the other side. Through a bulb tube, the volume of the bulb being greater than the Sprengel tube into which the air is aspirated by an india-rubber tube, which is closed with the finger as soon as the aspiration is started in this way, the aspiration is continued until the oil arrives in this bulb. The Sprengel tube is then separated from the bulb and left until in equilibrium with the exterior temperature, which is determined by the liquid neither expanding nor dilating in the widest tube. The oil is brought to the mark either by removing with filter paper the liquid in excess or in touching the capillary tube with a glass rod impregnated with the oil to be tested. The tube is closed with the glass stoppers and weighed. By bringing to a vacuum the weight found, the result gives exactly the specific gravity to the fourth decimal place. Generally the weight of the volume of oil is compared with that of the same volume of water at the same temperature, and in continental countries that is 15° C. (59° F.). British specific gravity bottles are graduated at 60° F. Such gravities are expressed as $\frac{15{\cdot}5^\circ\ \text{C.}}{15{\cdot}5^\circ\ \text{C.}}$ and $\frac{60^\circ\ \text{F.}}{60^\circ\ \text{F.}}$

When it is necessary to determine the specific gravity of solid fatty bodies, e.g. the mixed fatty acids of the drying oils, they are first melted so as to enable them to be drawn into the Sprengel tube; the latter is then immersed in a flask containing water, so that its horizontal branches lie in two nitches in the neck. It is covered with a watch glass and boiled in water. It is necessary to obtain a fixed temperature to leave the tube some 10 minutes in this atmosphere of steam. The tube is filled with oil to the mark under the above conditions and is confirmed by continuing the sojourn of the oil in the steam whilst making sure that the level does not vary.

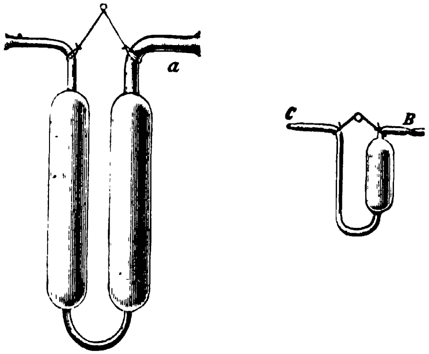

FIG. 46.—Sprengel's tubes.

Let P = weight of empty tube.
„ P^1 = its weight filled with water at 15° C. in the case of oils and 100° C. in the case of fats.
„ π = its weight full of oil.

The density is given by the formula $D\frac{\pi}{P^1} - \frac{P}{P^1}$.

Solidification-point.—The temperature at which linseed oil concretes into a solid fat is a useful indication. But, unfortunately, the figures of authorities differ here as in every other physical or chemical "constant". It is greatly to be feared that many of the determinations have not been made upon pure samples of linseed oil. It serves no good purpose to make elaborate preparations and precautions to secure accurate results with the samples tested if they be impure or even contain a notable proportion of fatty acid. Before taking the solidfying-point intended to form a standard for future reference and comparison, the oil in question should be pure and the fatty acids eliminated by treatment with alcohol, and all trace of the latter got rid of by gentle heating, avoiding oxidation. Linseed, walnut, and hemp-seed oils would appear to have much the same freezing-point, viz., - 27° C. (- 17° F.), whereas cotton-seed oil has a freezing-point, viz. - 2° C. (32° - 3·6 = 28·4° F.), very nearly that of water. But it must not be taken for granted that the freezing-points of mixtures of two or more oils can be calculated from the freezing-points of their ingredient oils. This would be a great mistake, and there is abundant evidence to show that mixtures of oils behave in this respect as abnormally as similar mixtures in the inorganic world, and just as mixtures of the carbonates of potash and soda melt at a temperature much lower than either carbonate does alone, so also does a mixture of cotton-seed oil stearic acid and

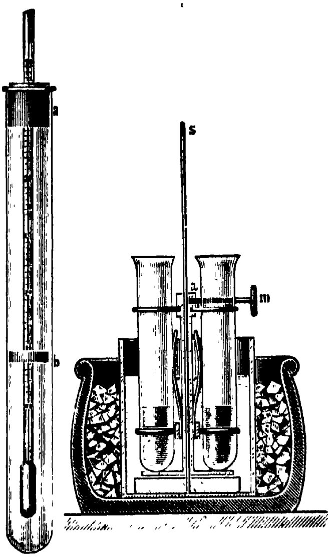

FIG. 47.—Apparatus for determining solidfying-point of linseed oil by use of a freezing mixture.

stearic acid from tallow melt at a temperature below that of either of these varieties of stearic acid. Again Jean was baffled in his attempt to determine the m.p. of oils like linseed by mixing them with a percentage of palmitic acid of known m.p., but possibly he might have succeeded better had he used ceresin of high m.p. The solidifying- or freezing-point of linseed oil is determined by freezing mixtures surrounding the tube containing the oil. The thermometer is inserted into the tube by means of a cork *a*; the thermometer is fitted with an agitator *b*.

The m.p. of the fatty acids from linseed oil, viz. 11° C., differentiates it from several other oils, especially cotton-seed oil, whose fatty acids solidify at + 28·5° to 30° C. But here again the utility of such data is negatived by the fact that, judging from analogy, the fatty acids from a mixture of the two oils in equal proportions would not be at all likely to yield a product with a freezing-point which would be the arithmetical mean of those of its constituents. Much information may be intuitively gained in regard to the solidification and m.p. of oils by observing the behaviour of the stock bottles and samples, filed away for reference, when a frost begins to set in, and again when the corresponding thaw ensues. Cotton-seed, olive, lard, and colza oils are all solid long before linseed oil, and the latter "thaws" much sooner than any of the others. The solidification-point is more useful in identifying individual oils than in detecting sophistication. However, it may be laid down as a general rule that the freezing-point of drying oils is much lower than non-drying oils, and although fish oils in many of their properties resemble drying oils yet in this respect they show a marked difference, the freezing-points of most fish oils being about 0° C., whereas linseed oil is - 27° C.

The data as to the solidification and melting-points of linseed oil are very conflicting. The difference in the source and the age cause a difference in composition, and the more linseed oil consists of a mixture of various bodies and the method of freezing, abrupt or gradual, and the oil stirred or not, the more will the results differ.

The Freezing Process of Eliminating Mucilage from Linseed Oil.—Dr. Karl Niegemann patented a process of purifying linseed oil for the manufacture of varnishes, which is essentially different from the customary methods employed. Raw linseed oil, when used for varnish-making, gives a product which becomes cloudy and opaque owing to the presence of albumen. According to the new process no heat is used to cause the albuminous matter to separate, the raw oil being, on the contrary, cooled to its freezing-point. For example, a sample of linseed oil whose solidfying-point is - 20° C. or 4° F. is cooled to that temperature and the mucilage separates in flocks just as it does when the oil is heated to 270° C. (518° F.). The oil is then warmed sufficiently to cause it to melt and become capable of being filtered, care being taken, however, that the temperature does not rise

SOLIDIFICATION-POINT OF THE PRINCIPAL OILS.

Oil.	Massie.	Braconnot.	Château	Fr. Chatin.	Various.
	Degrees C.	Degrees C.	Degrees C.	Degrees C.	Degrees C.
Sperm	—	+ 8	—	—	—
Olive	+ 2·5	+ 7	- 2·5	+ 2·75	+ 2 + 6
Whale	—	—	—	—	0 + 1 + 2
Cod-liver	0	—	—	—	1·0
Neatsfoot	0	—	—	—	1·5
Trotter	0	—	—	—	1·5
Lard	0	—	—	—	—
Arachis	+ 2	—	—	- 3	- 7
Cotton-seed	—	- 2	—	—	- 3
Rape	- 3·75	- 5	- 3·8	- 3·75	- 3·25 - 4
Sesame	- 5	—	—	—	—
Oleic acid	- 6 to 7	—	—	—	—
Colza	- 6	- 6	- 6·3	- 6·25	- 6·75
Hazel-nut	- 10	- 10	- 18·5	—	- 20
Sunflower	- 16	—	—	—	—
Grape-seed	—	—	—	—	- 16
Black mustard	- 1 to 2	—	- 17·5	—	0
Beech-nut	- 17	- 17	- 17·5	- 17·5	—
Castor	- 18	—	- 17·5	- 18	—
Poppy-seed	- 18	- 18	- 18·5	- 18	—
Camelina	- 18	- 18	- 18·8	- 18	—
Apricot	- 20	—	—	—	- 21 - 22
Almond	- 25	- 2·5 ?	- 2·3 ?	—	- 10 - 12
Hemp-seed	- 15	- 15	—	—	- 26·7
Linseed	- 15 to 20	—	- 27·5	- 27·6	—
Walnut	- 27	- 27·5	- 27·5	- 28	—
Pine	—	—	—	—	- 30
White mustard	—	—	—	—	- 17·5

SOLIDIFICATION-POINT OF LINSEED OIL AND ITS FATTY ACIDS.

Linseed Oil.		Fatty Acids.			
		Solidification-point.		Melting-point.	
Degrees C.	Observer.	Degrees C.	Observer.	Degrees C.	Observer.
- 16 after standing several days	Gusserow.	13·3	Von Huble.	17	Von Huble.
- 27	Château.	17·5	Allen.	24	Allen.
Melts at - 16 to 20	Glaesner.	16 to 17	De Negri & Fabris	Below 13	Dieterich.
Deposits stearine at - 25	Lewkowitsch.	19 „ 20·6 19 „ 19·4	Holde.	20 to 21	De Negri & Fabris.
		20·2 to 20·6	Lewkowitsch.		

above 0° C. or 32° F. It is then filtered, and an oil is obtained which does not again become opaque or cloudy, and which is suited for the manufacture of varnishes. The method possesses the advantage of removing the albuminous matter without increasing the percentage of free fatty acids. Niegemann very evidently omitted to reckon with the presence of solid glycerides naturally dissolved in linseed oil, viz. palmitin and myristin. The question then is whether he did not precipitate both these fats from the linseed oil along with the mucilage and how much, if any, such cold eliminated solid fats was retained on the filter along with the precipitated mucilage. Later on Lewkowitsch and others patented freezing processes for eliminating these solid glycerides from linseed oil, but the method did not pay, and the process was abandoned accordingly.

Effect of Cold on Linseed Oil.—It has been stated that an oil subjected to the action of cold remains permanently cloudy and breaks on heating to 270° C. (518° F.), even though the original oil did not behave in this way. The following tests were made by Andes with oil received from the oil-mill clear and transparent, giving no sediment on long standing, and on heating to 270° C. showing the characteristic change of colour, but not breaking or showing any dark coloured separation. Three samples of the above linseed oil were placed in large test tubes, filled to the top, and a thermometer fixed through a cork into each. The tubes were placed in a mixture of crushed ice and common salt. After 15 minutes the thermometers registered - 6° C. and the oil began to be cloudy. The temperature sank for two hours when it had reached - 16° C. The oil was now very thick, but not solid. All three samples behaved alike. A fourth sample of oil, in a similar cylinder, was placed in a freezing mixture of snow and calcium chloride. This sample was cooled down to - 31° C., and on standing at that temperature became quite solid, without the separation of any crystalline body. All four samples were now taken from the freezing mixture and brought into a warm room, where they were allowed to stand untouched for three days. All became quite clear as before, showing no solid or suspended matter, nor could they be distinguished in any way from the original sample. On heating to 270° C. they showed the normal coloration, without breaking. Pure linseed oil, therefore, will stand great cold without losing any of its normal properties, or suffering injury, notwithstanding statements to the contrary.

The Physical "Constants" of Linseed Oil and its Fatty Acids.—For any technical purposes hitherto known for which linseed oil is available fatty acids are much inferior if not quite unsuitable. Their melting point is far too low for candle-making on the one hand (even if the smell of the products of combustion did not debar it), and far too high for paint purposes; moreover, linoleic acid is a hydrated product whereas linseed oil only contains the anhydride of linoleic acid in combination with the glycerine. If we glance at the physical "constants" of raw linseed and the physical "constants" of the fatty acids derived from this same linseed oil as given in table, it will at once be seen that the original oil is quite a distinct substance from the free fatty acid derived from it. The original oil remains fluid at - 10 to - 20° C., that is to say 14° F. (18° F. below freezing-point). The freezing-point of the Fahrenheit scale is 32° F., and its zero is 32° F. below freezing; hence 20° C. = 36° F., and deducting 32° F. from 36° F. we get - 4° F. Now a substance like linseed oil which is still fluid at - 4° F. is quite a different substance altogether from one which is still solid at about 60° F. If the painter is working at 60° F. he very evidently cannot use linseed oil fatty acids as a vehicle for his paint, nor as a constituent of his varnish.

What has been said in regard to the melting-point of fats is equally true in regard to the solidification or freezing of oils, drying oils included. The first point to strike the observer is that most fatty solids begin to melt at a given temperature, and are not completely liquefied until a much higher temperature is reached. That would appear to be quite contrary to the laws of fusion according to which (1) every substance begins to melt at a determinate temperature which is invariable for each substance if the pressure is constant; (2) whatever may be the intensity of the source of heat from the moment it begins to melt the temperature ceases to rise and remains constant until the substance is completely melted. How then does it come about that drying oils escape the jurisdiction of such laws? It is due to several causes. Speaking chemically, drying oils are not pure, well-defined bodies but mixtures of several different pure well-defined bodies called glycerides, each of which has its own well-defined melting and solidification-points, and tends to melt at that point independent of all the other substances with which it is associated. But if that were the only stumbling-block matters would be much more simple than they are, and as the temperature was gradually raised we would see linolein, palmitin, myristin, stearine, etc., successively liquefy each with a fixed temperature as its own melting-point. However, matters do not arrange themselves so easily. This melting-point is not even now well determined for each of these glycerides and is liable to vary appreciably under circumstances as yet ill defined. But quite other causes intervene to modify greatly the phenomena, either to hasten or retard the melting-point. Much depends on the natural mixture of fatty bodies constituting any given oil. The less fusible substances tend to retain the more fusible by a sort of imbibition and the more fusible tend to dissolve the less fusible. The duel between these two tendencies leads within certain limits of temperature to the formation of a soft pasty state intermediate between the solid state and the liquid state, which may here be regarded as a state of imbibition of a solid mass by its saturated solution.

But some additional remarks are called for. The laws of solidification as given in textbooks on physics are generally enunciated thus: (1) Solidification takes place in the case of each substance at a fixed temperature which is exactly that of melting. (2) From the moment when solidification commences up to the time when it is complete, the temperature of the liquid remains constant. Now these laws are not so absolute as may be imagined and are subject to numerous exceptions. First of all the last part of the first law cannot be allowed to pass in the strict interpretation of its text. In fact if ice melts at 0° the water produced by this melting cannot resume the solid by the simple fact that the temperature remains at 0°, nor again if a piece of ice and liquid water be brought together and kept at 0° we do not simultaneously see the ice melt and the water freeze. It is therefore rational to suppose that if water melts at 0° water cannot freeze but at a lower temperature than 0°. However small may be the difference there is perforce one, and in a general manner the solidification-point is always lower than the melting-point; however near they may be in many cases they are always different. But in the case of natural oils and fats, cr even well-defined fatty bodies, pure triglycerides, this difference is peculiarly in evidence, for, in their case, there is always a very appreciable difference between the melting-point and the solidification-point of the same substance. Another well-known exception is that caused by superfusion, very frequent with fatty bodies: that is to say, where a substance cools down to an appreciable extent below its freezing-point without solidifying, a moment arrives when, under the influence of sudden vibrations or of some other known or unknown cause, the liquid solidifies all at once and its temperature rises to the freezing-point. There are, moreover, other remarkable exceptions to the laws of solidification and melting peculiarly applicable to oils and fats; they consist in variations induced by different conditions hitherto badly explained. One of the most remarkable depends on the temperature to which a substance has previously been brought before its solidification. For example, stearine, a well-defined body, melts according to different authors at 61 to 63° C., also up to 64·2 and even to 71° C. Now according to Duffy a stearine melted at 63° C., and heat continued to 65° C., solidified at 61° C., when reheated melted at 66·5° C., and when again solidified was found to resume its original melting-point of 63° C. Berthelot not only observed similar phenomena in the case of natural oils and fats but also in the case of synthetic glycerides. These variations in the melting and solidifying-point, sometimes influenced by the shape of the vessel in which the experiment is made, are always accompanied by considerable variations in density. There might therefore be some reason in accounting for these variations by molecular phenomena of polymerisation.

In any case, besides the unknown causes which intervene to vary these characteristics, there is one which must always be taken into account in connection with the fusion and solidifying-point of oils, and that is their low conductivity for heat, and, consequently, the slowness of the centripetal or centrifugal propagation of caloric through their mass.

In conclusion, it is easy to understand how the simultaneous action of these different causes may complicate the question of the melting and solidifying-points of oils and fats. It will not be surprising, therefore, to find very often considerable discrepancies between the solidifying-points of linseed oil and its melting-points after being solidified in the results of different experimenters according to the method adopted by each of them, and perhaps also according to the point of view he took up in making the experiment. Figures given as absolute for substances which in their properties are more or less heterogeneous mixtures cannot present a strictly definite melting-point and must only be accepted with great reserve.

It will be readily understood that this phenomenon may vary indefinitely according to the nature and proportion of the more or less well-defined fatty bodies (triglycerides) entering into the composition of the oil. But that is not all. Different substances may be found mixed together in a solid mass without being reciprocally soluble, and there may be imbibition or incorporation without solubility just as in the liquid state there may be emulsion and not solution. Now different substances may be found mixed together under these conditions with true fatty substances in natural oils and fats and must tend to slightly alter their melting-point. Finally, in certain cases there may occur between two bodies not mere admixture but true chemical combination; here then results a new body with a distinct melting-point from the previous two. This is more often the case than might be imagined, for in general a mixture of fatty bodies, or even of fatty acids, has a melting-point lower than that of the most fusible of its compounds, just as is the case with metallic alloys, which confirms the hypothesis of a chemical combination between them. However that may be, it has been found in a general way that every mixture which alters the melting-point of a body, lowers it in so doing.

Determination of the Molecular Weight of a Substance by the Cyroscopic Method.—This method, discovered by Raoult, consists in determining how far the freezing-point of a liquid product has been lowered by the solution in that liquid of a known weight of the substance, the molecular weight of which has to be determined. Let us examine this principle a little more fully, and let us take a well-known substance, as the product whose molecular weight is to be dissolved, viz. sugar, and a well-known liquid, viz. water, as the solvent, the lowering of the freezing-point of which is to be observed. When sugar is dissolved in water, the extent to which the freezing-point has become lowered is directly proportional to the weight of sugar dissolved; 1 part of sugar dissolved in 100 parts of water (bear in mind this is not a 1 per cent. solution which consists of 1 part of sugar in 99 of water) lowers the freezing-point about 0·058, i.e. the saccharine solution freezes at 0·058 instead of at 0° C., the freezing-point of pure water. Again, 2 parts of sugar dissolved in 100 parts of water depress the freezing by ·0116, 3 parts by 0·174.

But water is not a good solvent for numerous organic substances, many of which are, practically speaking, insoluble therein. In that case other solvents which are found to lend themselves to this purpose have to be used, bearing in mind that each organic compound has its own peculiar solvent, but some of these are unsuitable. The following is a list of the chief solvents used in cyroscopy :—

Solvents.	Freezing-point °C.	K.
Water	0	19
Acetic acid	14·8	39
Ethylenic bromide . .	9·6	119
Benzene	5·8	49
Nitrobenzene . . .	5·3	69
Phenol	39·0	76

It must, however, be borne in mind that hydroxylated substances in benzene solutions produce depressions which are too feeble by half. In such cases ethylenic bromide, nitrobenzene bromoform, etc., are substituted for benzene. Moreover, solvents which act chemically on the substance dissolved are avoided; thus acetic acid would not be chosen as a solvent for a phenol or an alcohol. In sufficiently dilute solutions of an appropriate solvent, other organic compounds than sugar behave similarly, and the lowering or depression of the freezing-point is (approximately) proportional to the number of molecules of the substance dissolved in a given weight of the solvent used and independent of the substance dissolved. If therefore we dissolve molecular proportions of different substances in a sufficient quantity of the solvent the depression of the freezing-point is the same in all the solutions. It evidently differs, however, with different solvents. That is to say, if the molecular weight in grammes of any substance be dissolved in 100 grammes of a given appropriate solvent, the depression of the freezing-point is a constant quantity K, termed the molecular depression of that process, Raoult's. Apparatus most frequently used consists of a cast-iron dish resting on a tripod, on the sides of which two vertical brass rods are riveted at the extremities of the same diameter. On one of these rods there moves a universal supporting ring which serves to keep in the centre of the dish a brass cylinder closed at its lower end. In this cylinder is a glass test tube, the outside diameter of which is slightly less than that of the cylinder; this test tube is intended to contain the liquid, solvent, or solution of which the point of solidification is to be determined; it is closed by a rubber cork pierced by three holes. There pass through the cork (1) A thermometer graduated into $\frac{1}{50}$ of a degree. (2) A very short glass tube into the orifice of which passes the stem of a platinum ring stirrer. (3) A wider glass tube, to allow the introduction if need be of a certain quantity of the solidified solvent. The platinum stirrer is furnished with a wire rolling on a pulley supported by the second brass rod. The different layers of the cooled liquid may thus be easily and constantly mixed. The test glass, previously dried and cleaned, is filled to two-thirds with the pure solvent. The cork is replaced and the thermometer introduced so that it does not touch the bottom and the bulb does not rise out of the liquid and remains within the axis of the ring of the stirrer; that done the test is placed in the cylinder and the dish is filled with crushed ice or ice and salt, taking great care that neither ice nor salt find their way into the brass cylinder. As soon as the operation begins the layers of liquid are continuously mixed by aid of the platinum stirrer, which should never come out of the liquid; a single to-and-fro motion can be given in a second. The column of the thermometer should never be lost sight of, especially when the temperature approaches solidification. At the moment when the solvent begins to crystallise the mercury remains stationary, then rises suddenly and again stops, to redescend afterwards when solidification is complete. This maximum temperature is noted and the experiment repeated a second time, by first lifting the test tube out of the cylinder to allow the solvent to regain the liquid condition. The two readings ought to agree to about $\frac{1}{100}$ of a degree. The solidification-point of the solvent having been determined, a solution is prepared of the substance to be examined in the same solvent; that is to say, in a portion of the liquid from the same bottle and withdrawn therefrom at the same time as the portion with which the previous determination has been made. The concentration of the solution should run between 3 and 5 parts per 100, so that the lowering of the freezing-point may be about 0·5 to 1·5. Its volume should be equal to that occupied by the pure solvent in the first experiment. It would thus be necessary to calculate previously the weight of substance and solvent to use in each particular case. The solvent is weighed in a flat-bottomed flask into which the weighed substance in a closed tube is likewise introduced. The flask is closed and the solution is effected without heating by gentle agitation. When the liquid is quite homogeneous it is introduced in whole or into the test tube which has previously been cleaned and dried, likewise the stirrer and thermometer.

Calculation: let P = weight of solvent, p that of the substance dissolved, c the lowering of the solidifying-point expressed in degrees; then the molecular weight M of the dissolved substance is given by the equation

$$M = K \times \frac{100 \times p}{P \times c}.$$

K is a constant particular to each solvent.

Certain solvents possess two constants K. The greatest of the wo is generally used.

Example.—Let us choose for our first example a substance soluble n water: 4·9818 grammes of cane sugar $C_{12}H_{22}O_{11}$, dissolved in 96·94 rammes of water, depressed the freezing-point by 0·925° C. Since 6·94 grammes of solvent contain 4·9818 grammes of substance P, he quantity in 100 grammes = 5·139 grammes. The constant K or water is 19, hence the molecular weight of cane sugar is found to e $\frac{19 + 5{\cdot}139}{0{\cdot}295} = 331$, the true value being 342.

Beckmann made some very unimportant alterations in Raoult's apparatus, but sufficient to enable the Germans and their too numerous followers in this country to claim that the depression of temperature is usually made with the aid of the apparatus devised by Beckmann. But Beckmann never devised his own apparatus, he only altered Raoult's. His instrument consists (1) of a large tube A about 1 inch in diameter and furnished with a side tube B, and closed with a cork C through which pass a stirrer *a* and a thermometer *b* graduated to $\frac{1}{100}$ of a degree. An exactly weighed quantity, about 25 grammes, of the solvent is placed in the tube, which is then filled into a wider tube D which serves as an air jacket and prevents a too rapid change in temperature. The apparatus is now introduced through a hole in the metal plate E into a vessel which is partly filled with a

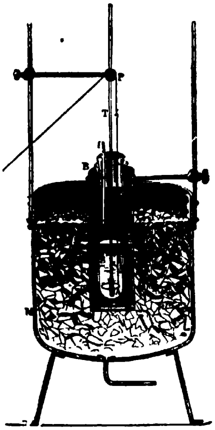

FIG. 48.—Raoult's freezing-point apparatus.

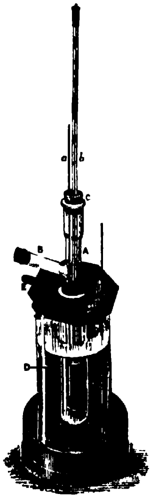

FIG. 49.—The same apparatus as modified by Beckmann.

liquid, the temperature of which is about 5° lower than the freezing-point of the solvent. The solvent in A being now constantly stirred the thermometer rapidly falls and sinks below the freezing-point of the solvent; the thermometer rises again, but then remains stationary at a certain temperature which is the freezing-point of the solvent. A weighed quantity of the substance is now introduced through the side tube B, and after first letting the solvent melt completely the freezing-point of the solution is determined as previously. The difference between the first and the second freezing is the depression.

The Specific Viscosity of Linseed Oil.—The specific viscosity is usually determined in this country by Redwood's Viscometer, on the

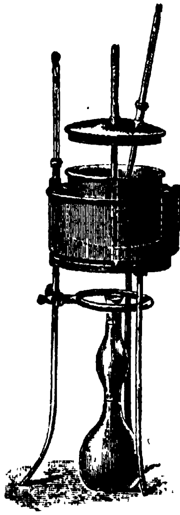

FIG. 50.

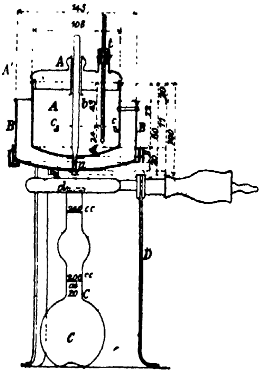

FIG. 51.

Continent and in the U.S.A. by Engler's. The former is described in vol. iii. of this treatise, pp. 423-5. In Engler's viscometer the operation is performed at 20° C. and the viscosity is compared with that of water at the same temperature. For linseed oil Crossley and Le Soeur found at 70° F. (21·1° C.) the viscosity of 8·33, but F. Bedford only found 6·75, and Ubbelhode at 20, 50, and 100° C. the viscosities 6·36, 3·2, and 1·6 respectively.

The consistency or body of thickened linseed oil varies with the use to which it is to be applied. An empirical test between the forefinger and thumb gives very often all the necessary information. Printers require both "thick" and "thin" or "medium" vehicles, or indeed a mixture of these. Other manufacturers are similarly situated, such as the manufacturers of oiled silk. An instrument designed to measure the body of the oil has been termed a consistence measurer, and for an accurate determination of the body of the oil is the best instrument to use. An expert oil boiler for printing ink vehicles, however, hardly needs such an instrument. It measures the period of time taken by an air bubble to rise through a column of oil in a glass tube. A cylindrical glass vessel, which may be closed by a carefully ground stopper, is filled so far with the oil to be tested that an exactly measured volume of air remains between the liquid and the inserted stopper. The glass cylinder is then inverted and the time noted which the air bubble takes to ascend from the bottom to

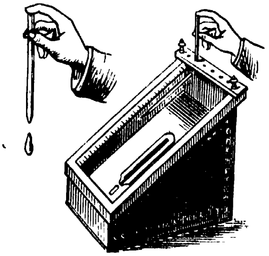

FIG. 52.—Apparatus capable of being heated for testing drying, viscosity, gumming, etc., of oils, with graduated scale to left and thermometer to right.

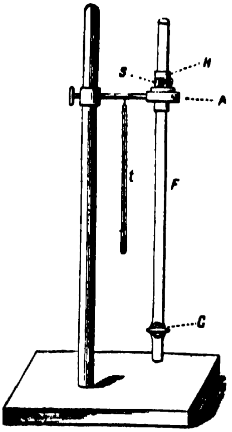

FIG. 53.—Valenta's apparatus for testing the viscosity of oils and printing ink vehicles.

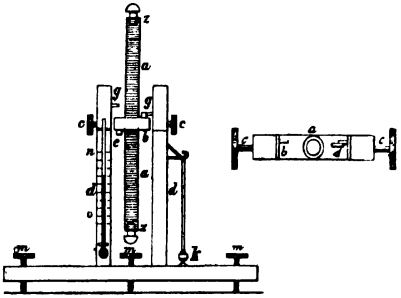

FIG. 54.—Apparatus for determining fluidity of thickened linseed oil.

the top. The glass vessel filled (see Fig. 54) consists of a tube *a* closed at each end by means of a glass stopper, and marked at *z*. *a* is attached to the axis *b*, with which it turns in the framework by means of pins; by removing the slides *cc*, *a* and *b* may be taken out. The reversing movement is stopped by means of the flaps *e* attached to the axis and the projections *g*, on the framework. The glass vessel, after it has been filled with the liquid to the upper mark *z* and closed, may be rapidly and accurately placed upside down, when the air bubble will rise. The framework *d* is provided with a plumb-line *k*, and three levelling screws *m*, so that it may be accurately placed in a vertical position with a thermometer to ascertain the temperature.

Viscosity of Boiled Linseed Oil and of Printing Ink Vehicles.— The ixometer consists essentially of a large vertical tube of 13 millimetres in diameter B. This tube ends in an overflow funnel F. Another vertical tube D of 5 millimetres diameter, also fitted with an overflow G, communicates with the first tube by a connecting pipe H of 8 millimetres interior diameter. In the centre of the tube D there penetrates a cylindrical steel rod E perfectly calibrated to the diameter of 4 millimetres. In fact this system forms in D an angular adjustment of 0·5 millimetre wide and 200 millimetres long. The whole can be introduced into a water-bath capable of being heated to a desired temperature,. The apparatus being ready for work the oil is placed in the funnel R fixed above B and the excess of oil is allowed to flow away through F. It is well at the start to incline the system at an angle of 45°, so as to run in a little oil to chase the air out of the annular. When the apparatus works satisfactorily and the oil is well at the temperature of the water-bath, a receiver which is under the funnel G is raised, and replaced by a graduated tube T, noting the time exactly at which the first drop of oil falls into this tube. The oil is collected for exactly 10 minutes. The tube is withdrawn and placed in the water-bath for 5 minutes, and the number of divisions obtained read. This number indicates the degree of fluidity of the oil at T° centigrade, that is to say, the number of c.c. of oil which flows out during an hour. Barbey's ixometer is so constructed that a pressure of 100 millimetres of liquid is kept at the fixed temperature of 35° C. Raw colza oil freshly prepared and drawn off clear marks exactly 100° of fluidity.

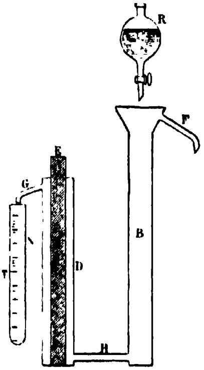

FIG. 55.—Barbey's ixometer with constant head of oil section.

FLUIDITY OR OUTFLOW PER HOUR IN CUBIC CENTIMETRES OF VARIOUS OILS.

	Specific Gravity.	Fluidity.
Alsatian mineral oil	0·927	67·2
American „ „	0·879	54
Russian oleo naphtha	0·912	15
„	0·906	50
„	0·896	130
„ (Mazout)	0·912	40—43·2
Vaseline	0·892	216
Oleic acid	0·909	138
Colza, crude, genuine, fresh syphoned off	0·9155	100
Colza, crude	0·915	84
„ refined for lamps	0·915	105
Rape	0·916	80·4
Ceylon cocoanut	0·920	160
Cochin (snow white)	0·925	180
Palm	0·918	126
Earth-nut, white edible	0·917	114
„ crude	0·920	104·4
Olive, fine tasted edible	0·9165	127
„ green (lubrication)	0·9160	125
„ „	0·918	105·6
Sesame, extra Jaffa	0·923	126
Cotton	0·9225	126
Ravison	0·921	110
Linseed, Calcutta	0·933	170
Neatsfoot	0·917	122
Horse-foot	0·9184	135
Trotter	0·916	116
„	0·917	98·4
Linseed, Bombay	0·935	143·4
„ Du Nord	0·936	144
Cod oil (brown)	0·928	155
Lard oil	0·916	120
Fish	0·927	135—160
Rosin	0·975	80
„	0·984	72
Castor-oil lubrication	0·964	13·2—15·0

Directions for Use.—Fill plugged container 4 with water to swage ring, and ascertain the time that 100 c.c. of water at 60° F. will take to pass through the jet of the container into the flask, which is graduated to this volume. This time is taken as the unit in reference to which the consistency or viscosity of the material to be tested is determined and numerically expressed. Thus if 100 c.c. of water at 60° F. take 22 seconds to pass through the jet, and the material under test be assumed to take 110 seconds, the latter will be said to have a relative viscosity of $\frac{110}{22} = 5$.

To take the viscosity of a given material:—

Having seen that the container and jet are perfectly clean, insert the plug in the jet and put on the cap which holds thermometer 1. Light the burner and, closing the door, raise the temperature of the

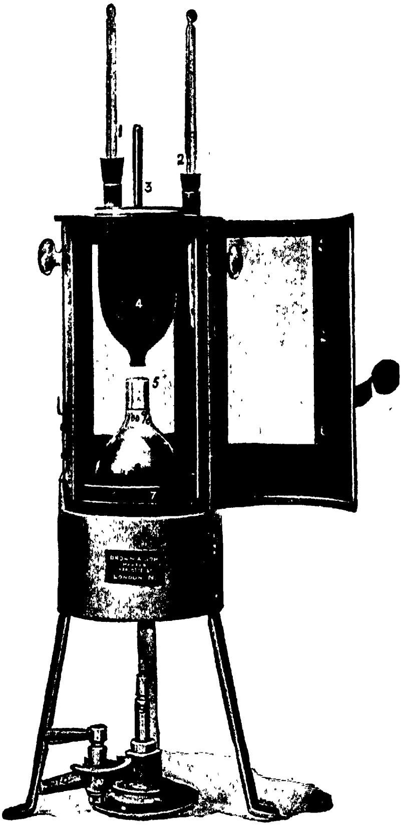

FIG. 56.—"R.E." viscometer (*Hutchinson*).

1, Thermometer immersed in material under test; 2, thermometer showing temperature of air-bath; 3, plug for closing and opening jet or outlet tube of container; 4, copper container with interior swage-ring marking capacity of 110 c.c., and removable phosphor-bronze jet; 5, mica windows for observations; 6, glass receiving flask graduated to 100 c.c.; 7, copper pan, removable, for catching possible overflow; 8, iron stand; 9, luminous burner for heating air-bath; 10, regulating tap having engraved quadrant for fine adjustment.

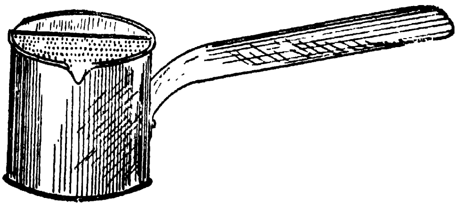

FIG. 57.

air-bath towards the point desired. While waiting until thermometer 1 approaches the same point, heat material to be tested in copper strainer (Fig. 57), stirring frequently. Removing the cap, next pour into the container the heated and stirred material up to the swage ring indicating 110 c.c. Replace cap, and as soon as thermometer 1 in the container is steady at the temperature fixed upon, withdraw the plug and note, by means of a stop watch, the number of seconds taken by the material to fill the flask to the mark graduated for 100 c.c.

Assessing Linseed Oil by the Colour Test Developed by a Drop of Sulphuric Acid on 10 Drops of Oil.

The Sulphuric Acid Spot Test for Linseed Oil.—This is the most valuable qualitative test for the purity of linseed and other oils. Yet it is conspicuous by its absence from most technical works on oils or is disposed of by a few words in passing. The apparatus required is simple: (1) Three or four glass rods rounded or dubbed; (2) a stoppered bottle containing concentrated sulphuric acid; (3) a white porcelain slab with several circular hollow depressions as shown in the illustration, or a plain porcelain slab will do, or even a plate of glass with a sheet of white paper underneath, but the circular depression plate is much to be preferred as the oils have a tendency to run into one another and it is difficult to avoid getting into a nasty mess when testing a series of oils. The circular depression for each oil avoids all this unpleasantness. Rubber bulb tubes are also used for spotting.

Process.—Put a number on each sample bottle of oil to correspond with the number of the depression on the plate. Then spot 10 drops of each oil to be tested from its bottle on to its corresponding depression on the plate. Dip one of the glass rods, which must be scrupulously clean, into the sulphuric acid bottle and carefully carry away on it as much as will spot 1 drop of acid, being careful not to drop the superfluous acid about the table. Two drops are generally necessary, one above the other. Place the rod in a beaker when done with. It must not be allowed to touch the oil. If it be desired to stir the oil another rod must be used. The 2 drops may often be spotted at once from the acid secured on the rod by one dip, but it is best to be content with 1 drop and to make a second dip into the bottle for the second drop. The rod must be allowed to drain sufficient for the purpose. The sulphuric acid may be spotted from a Mohr's burette with a glass stop-cock with greater ease and cleanliness. Pure linseed oil under sulphuric acid spot test behaves thus: The spot quickly assumes a yellowish tint, passing rapidly to orange, then to bright red, darkening gradually to brownish-black.

Oils detected in linseed oil by sulphuric acid spot test:—

1. *Rosin Oil.*—The importance and great value of this test merits a closer study than oil chemists bestow on it. Should linseed oil

contain only 5 per cent. of rosin oil the behaviour of the sample will show a marked deviation from the pure sample. It becomes brownish-red instantly and passes much more quickly to black than a pure sample, and the black coloration is always deeper than that of pure oil. Even smaller quantities than 5 per cent. of rosin oil can be thus detected. If fluorescence, smell, taste, gravity, and sulphuric acid spot test all point to rosin oil, it should now be determined by Allen's separate alcoholic saponification and ether extraction method (see p. 103), and very possibly it will be the only adulterant present.

2. *Whale Oil.*—As soon as the centre of a spot of pure whale oil is touched by sulphuric acid a rapid motion takes place from the centre to the circumference, chasing, so to speak, a grey coloration in front of it. The central spot, at first red, passes to brown-red, and, in a quarter of an hour's time, the whole spot becomes brownish-black. In testing linseed oil for whale or other oils in this way it is better to test simultaneously a standard sample of genuine linseed oil, a standard sample of genuine whale or other oil along with the oil to be tested, examining and comparing the colour effects. It must be borne in mind that there are many varieties of whale, each yielding its own peculiar oil, with its own behaviour to sulphuric acid.

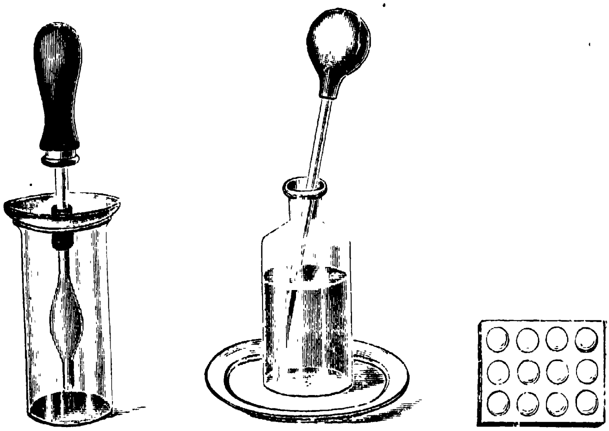

FIG. 58.—Apparatus for detecting rosin oil in linseed and other oils (sulphuric acid spot test).

3. *Cod Oil.*—The moment the drop of acid touches the oil red-violet striæ appear in the centre, which turn to dirty red and finally to black. Another description says the effect of the acid is to give an orange spot with a dark nucleus giving birth to a purplish floating crust which quickly browns. Stirring gives a bluish-purple, turning

to red and to brown. Violet to purple colorations are characteristic of fish-liver oils.

4. *Skate-Liver Oil* (density 0·928 at 15° C.).—Sulphuric acid spotted in centre causes beautiful violet striæ to swim about, which suddenly pass to bright brown. The centre of the spot is red, covered with brown striæ. A dirty grey aureole surrounds the circumference of the spot. (Gaseous chlorine does not darken the colour of this oil even after half an hour's contact.)

5. *Rape Oil.*—Before stirring gives a greenish-blue aureole. After stirring a bluish-green.—Elaidin test gives black mass.

6. *Hemp-seed Oil.*—The reagent gives a yellow spot where the acid has been dropped, the remainder of the oil turns greenish-blue, then a beautiful emerald green, with small brown striæ on the edges.

7. *Ravison Oil.*—This oil is known by its sharp pepper-like taste. The reagent gives a bluish-green aureole, which soon passes to dirty grey, leaving on the edges dark brown spots. The centre instantly becomes reddish-yellow, turning to bright brown.—Elaidin test gives black mass.

8. *Sesame.*—Only oil which gives characteristic bright red.

9. *Poppy.*—Yellow immobile spot with orange rings. Turns buff on stirring, finally brown-red with disengagement of gas.

10. *Walnut Oil.*—Yellow spot, which moves from one side to the other, producing quite an orange pellicle on surface of oil; stirring produces dark streaks and liberates gas bubbles.

11. *Mustard Oil.*—According to Lefevre, gives a dark yellow spot with fibrous streaks, inclining to orange, and a nucleus which rapidly darkens. On stirring it gives a red-brown colour. On the other hand, according to Heydenreich, black mustard oil behaves somewhat like rape, giving a greenish-blue both before and after stirring.

Assessing Linseed Oil by the Tetrabromide of Tin Test for Rosin Oil.—Tetrabromide of tin, $SnBr_4$ (made by dropping dry bromine through a separating funnel into a well-cooled glass flask containing granulated tin), gives a characteristic violet-red coloration in presence of rosin oil. It is equally delicate and characteristic a test for rosin oil in linseed oil as the sulphuric acid spot test. This test is due to Allen, and is a modification of Renard's stannic chloride $SnCl_4$ test.

These colorations do not as a rule interfere with the detection of rosin oil.

The Liebermann-Storch Acetic Anhydride and Sulphuric Acid Coloration Test for Rosin Oil.—Storch has adapted Liebermann's colour test for rosin acids for the detection of rosin oil in linseed and other oils. From 1 to 2 c.c. of the oil to be tested are agitated with 1 c.c. of acetic anhydride with the aid of a gentle heat. After settling and cooling the acetic anhydride is drawn off by a pipette and 1 drop of concentrated sulphuric acid added. A fine but fugitive violet coloration is imparted to the acetic anhydride if rosin oil be present in the oil tested. This test is especially applicable for testing mixtures of rosin oil and mineral oil and rosin. C. Harrison asserts that he obtains satisfactory results by the use of glacial acetic acid in place of acetic anhydride. Morawski obtained the undernoted colorations with the following oils:—

Oil.	Coloration.	Oil.	Coloration.
Olive	Light green.	Palm	Brownish-yellow.
Sesame	Greenish-blue, gradual.	Bone fat acids	,, ,,
Hemp	Green.	Whale stearine	,, ,,
Linseed	,,	Olein	,, ,
Cotton	,,	Crude olive acids	Light brown to dark green.
Arachis	Red-brown.	Herring	Cherry-red to brownish-black.
Rape	Greenish-yellow.	Sunflower	Blue violet to blue.
Castor	Yellowish.		
Coco-nut	,,		
Palm-nut	,,		
Beef tallow	,,		

Assessing Quality of Linseed Oil by its Flash or the Point at which it Gives Off an Inflammable Vapour. Gray's Flash-point Apparatus (Closed Test). Description.—This apparatus (Fig. 59) consists of a brass oil-cup *a*, of the same dimensions as the oil container used in Government Standard Petroleum Testers (Abel's). On this cup, which is set on a suitable stand, is placed a tight-fitting cap or lid. Through the lid a steel shaft passes, carrying on the top a small bevelled wheel *h*, the bevel of which is milled, and on the lower part two sets of stirrers, one of which is below the surface of the oil, and the other in the vapour space above. A horizontal shaft carried on two standards terminates at one end in a bevelled wheel *g*, which gears with the wheel *h*, and at the other end in a disc *c*, the outer rim of which is made of bone or other suitable non-conductor of heat, and on this disc is fixed a handle *b* for rotating the shaft. This horizontal shaft carries a collar *e*, from which there projects two small pins at diametrically opposite points. By sliding the shaft slightly to the right the bevelled wheels are drawn out of gear, and the pins projecting from the collar put in position for actuating the testing arrangement. On the lid proper there are three orifices, one immediately in front of the test-light *d*, and the other two at either side of it. Above the lid is the sliding cover *s*, in which there are two orifices corresponding to those on the fixed lid. When the bevelled wheels are in gear the sliding cover is held in its normal position by the spring at *p*, and the orifices in the fixed lid are covered. When the sliding cover is moved by bringing the pin *e* in contact with the pin *p* and turning the disc *c* about a quarter of a turn round, the orifices in it coincide with those on the fixed lid, and at the same time the test-light is depressed and brought into position for producing the flash when the requisite temperature has been reached.

In places where gas is not available, a good substitute to use for the test-flame may be obtained by passing a current of air or hydrogen through cotton-wool or other convenient medium saturated with gasoline or other light hydrocarbon spirit.

Process.—Fill the oil-cup *a* up to the mark inside with the oil to be tested, replace the cap, and insert the thermometer in the tube provided for it. Apply a light to the heating lamp, the heat from which may be applied either direct or through the medium of a convenient sand-bath. Light the test-jet also, and adjust flame to about $\frac{1}{8}$ of an inch in length. During the heating of the oil the stirrers should be moved at short intervals by turning the handle *b* several times. The more rapidly the oil is heated the oftener the stirrers should be rotated. When nearing the point at which the oil is expected to flash, it is advisable to reduce the rate of heating in order

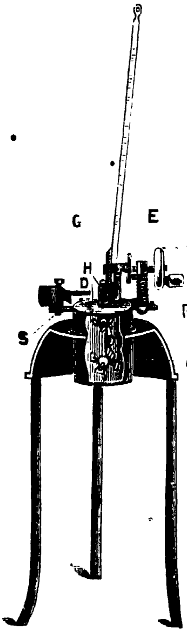

FIG. 59.—Gray's flash-point apparatus for linseed oil (open test).

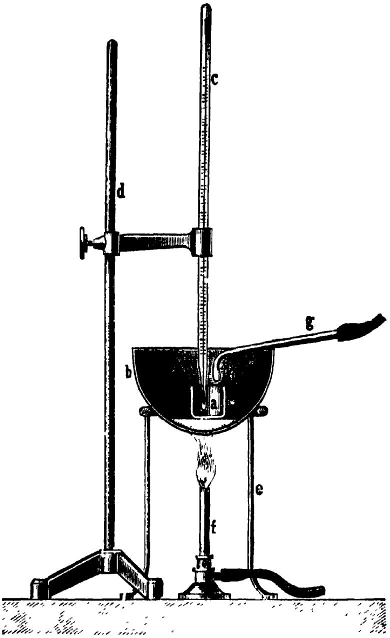

FIG. 60.—Apparatus for determining flash-point of linseed, etc., oils (closed test).

that the observations may be more readily and accurately made. If necessary, a rough test may be performed first, to give some indication of the temperature at which the oil is likely to flash. Observations may be taken every degree or half degree, a few turns of the stirrer being given between each test. The rate of heating is immaterial provided it is not too rapid to allow of readings being taken. A convenient time is 10 to 20 minutes.

COMPARISON OF FLASH-POINT STANDARDS OF DIFFERENT COUNTRIES.

Country.	Apparatus.	Principle.	°C.	°F.
America . . .	Taghabue and Saybolt tester	Close and open	35	95
Belgium	Gramer's	Close	—	—
Denmark . . .	Danish	Open	40	104
Germany	Abel Pensky's	Close	21	69·8
Great Britain . . .	Abel's	,,	22·78	73
France	Gramer's	,,	35	95
Holland	Porrischer's	,,	40	104
Japan	Burning test	,,	46	114·8
Austria	Abel Pensky's	,,	21	69·8
Russia	—	—	—	—
Roumania . . .	—	—	—	—
New York State . .	Tagliabue's	Close	37·77	100
Sweden	Danish	Open	40	104
Zurich	Abeljanz's	,,	34	93·2
Italy	—	—	—	—

Index of Refraction.—The index of refraction of oils, fats, turps, white spirit, etc., is deserving of more trade attention consequent on the ease and rapidity in making determinations, a few minutes sufficing for the whole operation. By the use of this instrument oils may be sorted out and mixtures detected. It is certain that anyone becoming habituated to the method will never consider an oil laboratory equipped without one or other of the instruments herein shortly described.

The Abbé refractometers, by virtue of their extraordinary simple manipulation (the refractive index $n/_{\text{D}}$ being read off directly on a graduated circle after a single movement requiring no particular skill) and their extensive range of measurements, embrace refractive indices from $n/_{\text{D}} = 1·3$ to $n/_{\text{D}} = 1·7$. The refractive index of linseed oil at a temperature of 15° C. may be found to be about 1·48140 and that of rosin oil about 1·535 to 1·549. The refractometer is mainly composed of the double prisms A, B, which contain the fluid, and may be rotated on a horizontal axis by means of an alidade, J. F is a telescope for observing the line of total reflection which is formed in the prism, S is the sector rigidly connected with the telescope on which are engraved divisions representing refractive indices.

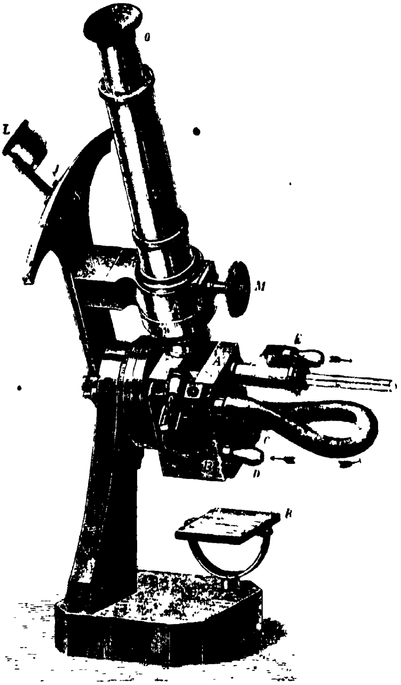

FIG. 61.—The Abbé refractometer with heatable prisms. Model I.

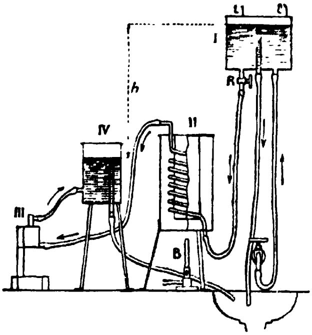

FIG. 62.—Heater and water pressure regulator.

In taking refractive index of liquids, it is convenient to make measurements at a fixed temperature, e.g. 20° C. The figure on p. 153 exhibits means of causing a heated current of water to circulate about the prisms.

Jean's oleo-refractometer is also employed for oil determination. Descriptions of the instrument are to be found in publications, and for brevity's sake are omitted.

Fery's Refractometer.—This instrument has the advantage over Jean's oleo-refractometer in not requiring a certain liquid oil as type or standard.

Theory of Fery's Refractometer.—Its theory is simple. It rests on the following facts. In a liquid prism of small angle the deviation is proportional to $(n - 1)$, n being the index of the liquid contained in the prism. In fact, if the angle A (Fig. 63) is small, ir, $i'r'$ are also small when the prism is in the vicinity of its minimum deviation, which is realised in the apparatus.

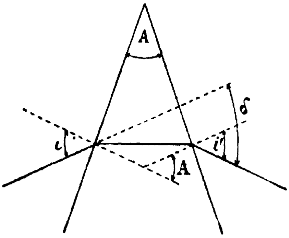

Fig. 63.

We then have: $A = (i - r) + (i' - r')$.

But given the smallness of the angles $n = \frac{i}{r}$.

Hence $i = nr$ and $i' = nr'$.

Therefore $\delta = r(n - 1) + r'(n - 1)$.

And as $(r + r') = A \qquad \delta = A(n - 1)$.

If we annul the deviation of this prism by the plano-convex lens L, the glass of which has an index N, we get for this latter

$$-\delta = -a(N - 1),$$

a being the angle at the point where the ray deviated by the prism just meets it. At this point, therefore, we have the relation

$$A(n - 1) = a(N - 1).$$

Hence $$n - 1 = a\frac{N - 1}{A}.$$

But it is easy to show that in such a lens the angle α at the point in question is very perceptibly proportional to the distance δ (Figs. 64, 65) which separates it from the optic centre O. We in fact get

$$\delta = K \sin \alpha$$

or for small angles $\delta = K\alpha$.

By replacing α in [1] by its value $\frac{\delta}{K}$ drawn from this latter equivalence, we find

$$(n = 1) = \delta \frac{N - 1}{AK} = K'\delta$$

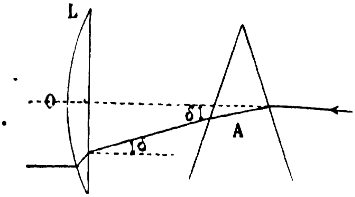

Fig. 64.—The index of refraction.

by causing the constants NA and K of the apparatus to enter into the constant K'. The angle A chosen to constitute the prismatic cell of the apparatus is small enough for the error due to the substitution of the arcs for the sinus in the preceding formula only to produce an error lower than the last decimal place shown by the Vernier.

Description of the Instrument.—The cell containing the liquid to be examined consists of a hollow prism of a suitable angle, the faces of which are also prismatic, but so arranged that the whole forms a

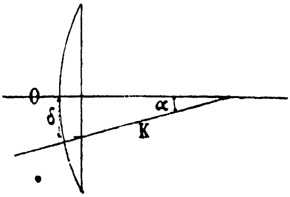

Fig. 65.—The index of refraction.

system of parallel faces *a*, *b*, *c*, *d*. The three prisms forming the cell to contain the liquids under examination are cemented together in such a way as to resist all solvents and are mounted in a metallic lining carrying two horizontal slits 3 millimetres in height. The lower slit lets light through the bottom of the cell and thus traverses the whole of three solid prisms acting like a blade with three parallel faces, these three prisms being made from the same glass, which is a special crown glass perfectly resistant to chemical reagents. The upper slit receives the rays which traverse the liquid, it is at the top of this slit where the reservoir which holds the bent thermometer *t* carried by the ground glass lid of this cell is fixed. This first cell is placed in a second cell MNPQ, all metal except the two larger sides MN and PQ formed by the plano-convex compensation lens, the

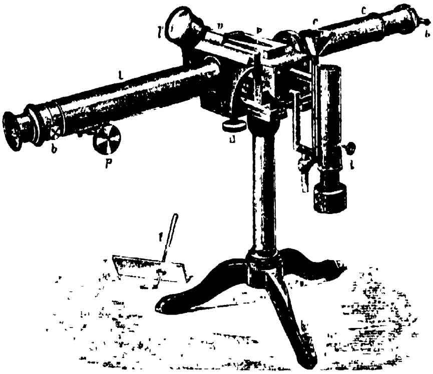

Fig. 66.—Fery's refractometer.

curved face of which is turned towards the exterior. The space included between the two cells must be filled with water, which is easily done through a funnel *c*, visible on the profile view of the whole instrument. There must be water between the two cells when the instrument is being regulated or when an observation is being

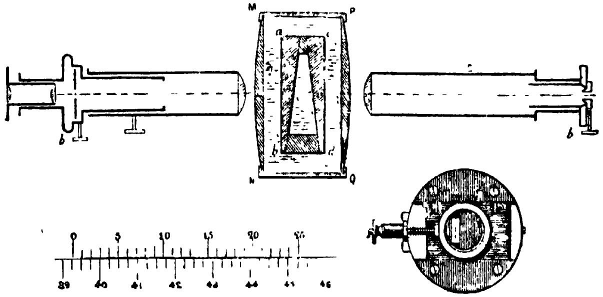

Fig. 67.—Fery's refractometer: Vernier, etc.

taken. It is the presence of water—which, however, plays no optical rôle in the measurements, for it forms a double plate with parallel faces—which ensures the constancy of the central cell and allows of it being raised to the desired degree by aid of a small lamp *l* which heats a thermo-siphon. Water may be replaced by any other fluid if need be, e.g. for determining indices below 0° C., without fearing any change in the readings. The central cell which slightly overlaps the heating cell is closed by a ground glass lid carrying the bent thermometer *t*. The exterior cell is fitted with a metallic lid pierced by a rectangular opening giving a passage to the central cell. The aggregate of the two cells borne by a slide may be displaced perpendicularly to the optical axis of the instrument determined by the reticula slit of the collimator C and the reticula in the form of a St. Andrew's cross of the lens L. These two reticulæ are mobile by means of studs *b*, *b′*. In its motion the exterior cell brings in its train a Vernier V and a magnifying glass *l′* in front of a fixed scale, by which its displacement can be measured to $\frac{3}{100}$ of a millimetre corresponding to $\frac{1}{10,000}$ of an index.

Description of the Vernier.—The scale is divided from 1·33 to 1·59, but not to overload the figuring, only the two first decimals are indicated. Each of these large divisions which represent almost 4 millimetres is divided into 4 parts. Each of its subdivisions represents $\frac{25}{10,000}$ or 0·0025. The Vernier is itself divided into 25 parts, the total length of which represents 24 small divisions of the scale.

It is therefore read thus, according to the example shown in Fig. 67: 39 large divisions plus 1 small division, which gives 3·925. We further read on the Vernier that it is the division 4 which coincides. The index is therefore 1·3929.

Regulating the Apparatus and Determining the Index.—The central cell being in position and the exterior cell filled with water up to the superior level of the liquid to be examined, to be certain of securing uniformity of temperature of the latter the two cells are closed by their respective lids and the height of the thermometer so that its reservoir is visible through the upper slit in the cell. The bench-marks of the slit of the collimator C are made to coincide by means of the stud *b′* and the index of the glass of the cell is caused to be marked on the Vernier by means of the stud B, an index which serves as a starting-point and which is engraved on each instrument. The index of glass is not affected by the temperature or at least the variations only affect a decimal point very far removed from what it is desired to reach. The reticula in the form of a St. Andrew's cross which is carried by the magnifying glass is adjusted by drawing the eyepiece. Then the vertical reticula of the collimator is adjusted by working the pignon P of the magnifying glass, the apparatus being illuminated by monochromatic sodium light. Finally, by means of the regulating stud *b* of the eyepiece the vertical reticula is made to coincide with the centre of the cross. There should exist no parallax between the centre of the St. Andrew's cross and the vertical reticula of the collimator when the eye is displaced near to the eyepiece.

The following instructions for the adjustment of the instrument should be obeyed: Once the instrument is regulated the stud B should only be used to take measurements. In order to do so the liquid to be examined is placed in the central cell if it be not there already, for its presence in no way hinders the adjustment of the instrument. When the temperature of this liquid indicated by the thermometer which dips into it is quite stationary, the stud B is turned until a new image appears in the field of the telescope. This image is formed by the rays which have traversed the horizontal upper slit of the central cell. It is brought to coincide with the reticula of the telescope as is done with the image of the glass of the central cell and nothing further remains to be done except to read the index on the scale of the instrument. Thus regulated, the instrument works between 1·330 and 1·5326. This adjustment is sufficient for the majority of liquids, saline solutions, fatty oils. If, however, it be seen that the index is not comprised between these limits, it is very easy to measure it; for that purpose, the regulating point given by the glass index is displaced to a known extent; if, for example, in an instrument, the glass of which has an index of 1·5126, it be desired to take the refractive index of carbon disulphide which is about 1·634, the bench-marks of the reticula carrying slit of the collimator are made to coincide by means of *b*′, there is caused to be marked on the Vernier 1·3726 by means of the stud B, and the reticulæ are then made to coincide by manipulating the stud *b* of the eyepiece. The magnitude of the scale of the instrument has been increased by 0·14 and the instrument works up to 1·6726. It will suffice to bear in mind that all the readings must be increased by 0·14, the point of departure having been displaced to that extent. If, therefore, 1·5227 was found 0·14 would be added, and we would get the index sought, 1·6627.

N.B.—The point of departure may be displaced between 1·3726 and 1·5126 by the quantity required to find the desired index.

Determination of indices at temperatures different from the ambient temperature. The following precautions must be taken if it is desired to work at a temperature above that of the laboratory. The lamp *l* is lit, the flame adjusted very low, the brass tube making a draught, and to which is brased a copper tube of small diameter forming a thermo-siphon, heats itself rapidly, an active circulation of the liquid is produced. The movements of the thermometer are watched and the lamp is extinguished when the temperature is 0·5 below what it is desired to reach. The thermometer continues to rise very slowly, then remains stationary before redescending. That is the moment chosen to make the determination. At that moment, in fact, equilibrium of temperature is completely established between the different media traversed by the ray of light. Working otherwise, delay might occur between the indications of the thermometer and those of the refractometer, in consequence of which one finds at the same temperature a higher index during heating and a lower one if the cooling be too rapid. It may happen that the index of the liquid is very near that of the cell; in that case the two images of the vertical reticula are superimposed and their measurement is difficult. In one experiment M. Ch. Fery found a body commercial, eugenol, the index of which at the temperature of the experiment was exactly the same as the glass of the cell. The two images absolutely coincide and the cell may be displaced through its entire length without finding a second image. In that case it suffices to counterbalance (bascule) a screen not shown in the figure in front of the lower slit corresponding to the glass, and the image of the liquid subsists alone. In fact, if a determination be made on a fluid which is a very bad conductor of heat like carvacrol, which placed in the cell has a syrupy appearance, an image cannot be obtained. It must be left for several hours for equilibrium of temperature to supervene, or what is more simple, heat is applied, and it is left to cool very slowly until it reaches the desired degree at which the index is to be taken. Determinations may thus be made of the index of refraction at different decreasing temperatures.

INDEX OF REFRACTION.

The following results are given for the purpose of comparing that of linseed oil with other oils:—

INDEX OF REFRACTION OF RAW LINSEED OIL.

Strohmer at 14° C. = 1·4836
,, at 16° C. = 1·4834
Thorner at 60° C. = 1·4660
Tolman and Triunson at 15·5° C. = 1·4831
Harvey at 20° C. = 1·4800—1·4812
Procter and Holmes at 15·5° C. = 1·4817—1·4825
U.S.A. at 25·5 = 1·4795—1·4798

INDEX OF REFRACTION OF CERTAIN OILS. (FERY.)

Index determined at 15°, correction 0·00037 at 15° C.			
Earth-nut, refined	1·47325	Trotter	1·47045
,, ,, crude	1·47315	Horse-foot	1·47095
Olive, Tunis	1·47215	Castor	1·47990
,, Kabylie	1·47015	Almond, sweet	1·47410
,, edible	1·47130	Cotton	1·47440
,, fine	1·47070	Black mustard	1·47490
Walnut	1·47160	Lard (oil)	1·47195
Poppy	1·47730	Oleic acid (sap.)	1·46245
Sesame, crude	1·47490	Whale (St. Vincent)	1·47505
,, refined	1·47400	,,	1·47925
Linseed	1·48140	Cod-liver, Hogg	1·48 00
Neatsfoot	1·47550	,, blonde	1·48885

RAW LINSEED OIL IN BUTYROREFRACTOMETRIC DEGREE.

	No. of Samples.	°C.	Refraction.
M. Weger, Zeitschr. f. angew. Chem., 1899, **12**, 298	6 4	25° 40°	80·2—81·5 71·4—72·5
J. van Itallie, Pharm. Weekblad, 1903, **40**, 106	6	25°	82·0—86·5
B. Sjollema, Zeitschr. f. Unters. d. Nahr.- u. Genu., 1903, **6**, 631 . .	15	15°	87·0–91·6
Thomson und Dunlop, Analyst, 1906, **31**, 283	5	25°	81·0—85·5
H. J. F. de Vries, Chem. Weekblad, 1908, **5**, 555	7	15°	87·3—91·8
Olig. und Brust. Zeitschr. f. Unters d. Nahr - u. Genu., 1909, **17**, 561 .	1	25°	80·0

The following are indices of refraction at 15° C. of linseed oil, and of substances which may be present in it as adulterants or otherwise :—

Oil.	Refractive Index.	Oil.	Refractive Index.
Linseed . . .	1·484 to 1·488	Turpentine . .	1·464 to 1·474
Cotton-seed . .	1·475	Rosin (Colophony) .	1·548
Rosin oil . . .	1·535 „ 1·549	Maize . . .	1·4765
Mineral . . .	1·438 „ 1·507	„ . . .	1·478 (at 20° C.)
Fish . . .	1·480		

REFRACTION OF PURE AND IMPURE DRYING, ETC., OILS IN OLEO-REFRACTOMETER DEGREES WITH JEAN'S REFRACTOMETER.

	Index of Refraction.	
Raw linseed oil—laboratory standard sample	+ 53°	= 1·48075
Refined raw linseed	+ 49°	= 1·47975
Raw linseed + 20 per cent. rosin oil .	+ 67°	= 1·48425
„ + 20 „ hemp-seed oil	+ 47°	= 1·47925
„ + 20 per cent. mineral oil	+ 17°	= 1·47175
Poppy (*œillette*) oil	+ 29°	= 1·47475
„ „ old	+ 35°	= 1·47625
„ (*pavot*) Calcutta oil	+ 27·5°	= 1·47437
„ „ „ old . . .	+ 33°	= 1·47575
Hemp-seed oil	+ 30° to 32°	= 1·475 to 1·4755
Walnut oil	+ 36°	= 1·4765
Ravison „	+ 25°	= 1·47375
Colza „	+ 17° to 18°	= 1·47175 to 1·4720
Rosin[1] „	+ 78°	= 1·48625

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[1] With some samples the whole field of the refractometer is black.

REFRACTION OF PURE AND IMPURE LINSEED OIL IN BUTYRO-REFRACTOMETER DEGREES.

	Refractometer Number at 20° C.
Pure linseed oil (raw)	80·5 to 82·2 = 1·47875
„ „ (boiled)	80·5 „ 84·2
Linseed oil + 20 per cent. rosin	above 100·0
„ + 10 „ „	94·5 = 1·48675
„ + 5 „ „	88·4
„ + 20 „ „ oil	above 100·0
„ boiled + 20 per cent. rosin oil	„ 100·0
„ „ + 10 „ „	92·7
„ „ + 5 „ „	88·2
„ „ + 15 „ cotton-seed oil	78·7
„ „ + 15 „ rape oil	79·1
„ + 10 per cent. mineral oil	89·6
„ boiled + about 30 per cent. of manganese rosinate	84·9

COMPARISON OF REFRACTIVE INDEX WITH OLEO-REFRACTOMETER AND BUTYRO-REFRACTOMETER AT 22° C.

Refractive Index.	Oleo-Refractometer Degree.	Butyro-Refractometer.	Refractive Index.	Oleo-Refractometer Degree.	Butyro-Refractometer Degree.	Refractive Index.	Oleo-Refractometer Degree.	Butyro-Refractometer.
1·46250	− 20	54·8	1·47100	+ 14	68·0	1·47950	+ 48	82·0
1·46275	− 19	55·1	1·47125	+ 15	68·3	1·47975	+ 49	82·4
1·46300	− 18	55·6	1·47150	+ 16	68·7	1·48000	+ 50	82·9
1·46325	− 17	55·9	1·47175	+ 17	69·1	1·48025	+ 51	83·2
1·46350	− 16	56·3	1·47200	+ 18	69·5	1·48050	+ 52	83·8
1·46375	− 15	56·6	1·47225	+ 19	69·9	1·48075	+ 53	84·1
1·46400	− 14	57·1	1·47250	+ 20	70·3	1·48100	+ 54	84·6
1·46425	− 13	57·4	1·47275	+ 21	70·7	1·48125	+ 55	85·0
1·46450	− 12	57·9	1·47300	+ 22	71·1	1·48150	+ 56	85·5
1·46475	− 11	58·2	1·47325	+ 23	71·4	1·48175	+ 57	85·9
1·46500	− 10	58·6	1·47350	+ 24	71·9	1·48200	+ 58	86·4
1·46525	− 9	58·9	1·47375	+ 25	72·2	1·48225	+ 59	86·7
1·46550	− 8	59·4	1·47400	+ 26	72·7	1·48250	+ 60	87·3
1·46575	− 7	59·7	1·47425	+ 27	73·0	1·48275	+ 61	87·6
1·46600	− 6	60·2	1·47450	+ 28	73·5	1·48300	+ 62	88·2
1·46625	− 5	60·5	1·47475	+ 29	73·8	1·48325	+ 63	88·5
1·46650	− 4	60·9	1·47500	+ 30	74·3	1·48350	+ 64	89·1
1·46675	− 3	61·2	1·47525	+ 31	74·6	1·48375	+ 65	89·4
1·46700	− 2	61·7	1·47550	+ 32	75·1	1·48400	+ 66	90·0
1·46725	− 1	62·0	1·47575	+ 33	75·5	1·48425	+ 67	90·3
1·46750	0	62·5	1·47600	+ 34	76·0	1·48450	+ 68	90·9
1·46775	+ 1	62·8	1·47625	+ 35	76·3	1·48475	+ 69	91·2
1·46800	+ 2	63·2	1·47650	+ 36	76·8	1·48500	+ 70	91·8
1·46825	+ 3	63·5	1·47675	+ 37	77·2	1·48525	+ 71	92·1
1·46850	+ 4	64·0	1·47700	+ 38	77·7	1·48550	+ 72	92·7
1·46875	+ 5	64·3	1·47725	+ 39	78·1	1·48575	+ 73	93·0
1·46900	+ 6	64·8	1·47750	+ 40	78·6	1·48600	+ 74	93·6
1·46925	+ 7	65·1	1·47775	+ 41	78·9	1·48650	+ 75	94·0
1·46950	+ 8	65·6	1·47800	+ 42	79·4	1·48675	+ 76	94·5
1·46975	+ 9	65·9	1·47825	+ 43	79·8	1·48700	+ 77	94·9
1·47000	+ 10	66·4	1·47850	+ 44	80·3	1·48725	+ 78	95·4
1·47025	+ 11	66·7	1·47875	+ 45	80·6	1·48750	+ 79	95·8
1·47050	+ 12	67·2	1·47900	+ 46	81·2	1·48625	+ 80	96·3
1·47075	+ 13	67·5	1·47925	+ 47	81·5	—	—	—

Refraction of Linseed Oil Mixed Fatty Acids.—Determinations are few. Thörner found a refractive index of 1·4546 at 60° C., whilst Olek and Burst found the butyro-refractometer degree of 56·9.

CHEMICAL AND PHYSICAL DATA OF PURE AND IMPURE BOILED LINSEED OIL.

	Butyro-Refraction at 25° C.	Polarisation.	Iodine Number.	Saponification Number.	Saponification (Turbidity) Test.
Litharge boiled oil 1	84·1	Feebly −	163·0	188·9	Clear
,, ,, 2	84·2	,,	167·1	—	,,
,, ,, 3	84·1	,,	165·0	—	,,
,, ,, 4	82·8	,,	167·5	188·4	,,
,, ,, 5	82·9	,,	162·3	188·7	,,
Manganese boiled oil 1	80·6	,,	172·1	188·9	,,
,, ,, 2	84·0	,,	170·4	186·1	,,
,, ,, 3	82·9	,,	167·7	190·2	,,
,, ,, 4 with 3 p.c. rosin oil	84·9	± O	164·8	185·4	Slightly turbid
Pure linseed oil	80·6-84·2	Feebly −	160-180	180-190	Clear
Litharge boiled oil 6	95·8	Strongly +	143·6	160·8	Quite turbid
,, ,, 7	96·3	,,	158·3	169·2	,,
,, ,, 8	89·6	,,	154·7	169·3	,,
,, ,, 9	91·9	,,	153·4	167·5	,,
Manganese boiled oil 5	90·0	,,	161·1	163·3	,,
,, ,, 6	over 100·0	,,	129·8	163·6	,,
Boiled oil + 20 p.c. rosin	,, 100·0	Slightly +	Acid number 45·6	197·6	Slightly turbid

It will be seen from the preceding table that, if a sample of raw or boiled linseed oil, examined at 25° C., is found to give a butyro-refractometer number greater than 84·5, it is open to the suspicion of containing an admixture of rosin, rosin oil, metallic rosinates, or mineral oil. On the other hand, if the butyro-refraction falls below 80, then additions of poor drying or non-drying fatty oils must be looked for. Very small percentages are not detected by the butyro-refractometer, but such are not likely to occur in practice.

The above table shows in how far the refractometer test coincides with the results of chemical analysis.

INDICES OF REFRACTION OF DIFFERENT VEGETABLE OILS IN DESCENDING ORDER.

Oil.	15° C.	22° C.
Linseed	1·4814	1·4788
Camelina	1·4806	—
Castor	1·4799	1·4773
Hemp	1·4777	—
Poppy	1·4773	1·4747
Maize	1·47665	—
Walnut	1·4762	—
Mustard	1·4749	1·4723
Rape	1·4748	—
Colza	1·4745	—
Beech	1 4745	—
Cotton	1·4744	1·4718
Almond	1·4741	1·4715
Sesame	1·4740	1 4714
Earth-nut	1·4732	1·4706
Hazel-nut	1·4716	1·4690
Olive	1·4705	1·4680

REFRACTION OF MARINE ANIMAL OILS.

	15° C.	22° C.
Cod-liver oil, pale	1·4833	1·4807
Japanese fish oil	—	1·4805
Fish oil	1·4793	—
Seal ,,	1·4784	—
Shark-liver oil	1·4775	—
Whale oil	1·4750	1·4724
Sperm ,,	1·4665	—

REFRACTION OF MINERAL OIL.

		15° C.
Russian	D—0·9066	1·5012
	D—0·908	1·4992
American	D—0·910	1·5111
	D—0·883	1·4894
Valvoline	Russian	1·5015
	American	1·4920
Rosin oil		1·5126-1·5615

In 1895 Hefelmann and Mann used the Zeiss butyro-refractometer for testing boiled oil and found that the refraction of an adulterated boiled linseed oil was from 80·6 to 84·2 at 25° C. Weger, however, showed in 1897 that these figures were unreliable except for freshly made boiled oils, or boiled oils which have been carefully kept from contact with the air, and which had not been heated for long during their manufacture, and not to a higher temperature than 180° C. For such he confirmed Hefelmann and Mann's results fully. He showed that oxidation and the use of high temperatures in manufacture greatly increased the refraction of boiled oil, and in many cases to 97 or even 99 after 18 months' exposure to the air. The influence of temperature suggests that the refractometer might be used to distinguish a boiled linseed oil, made drying by high temperature, i.e. by heating over a naked fire, from one made drying by dissolving siccatives in it at a comparatively low temperature. Unfortunately, the differences are not sufficiently great, and the expectation has not been realised. Consistency and smell are still the best tests.

Von Neander's values of the normal refraction are from 87 to 89, considerably above Hefelmann's therefore, and if such a standard were adopted, Hefelmann and Mann's figures would have to be taken as showing adulteration. As Weger has shown, however, Dr. Von Neander may have been experimenting with oxidised or highly heated oils. The use of monochromatic light, e.g. yellow sodium light instead of ordinary diffused light, in the refractometer tests has been recommended. In this way the refraction may be read to a fraction of a degree. The following is the result of experiments conducted in the way suggested (R = refraction). A mixture of 59·7 per cent. linseed oil (R = 81·1) with 50·3 per cent. of rape oil (R = 67·2) gave at the same temperature of 25° C. (R = 75°), and one of 73·9 and 26·1 per cent. respectively (R = 77°). To use these results in determining an adulteration with rape oil, it is not necessary to calculate the indices of refraction as Von Neander does. The angles can be used themselves. The equation will be, if

a = per cent. of adulterant present.
x = refraction of pure linseed oil.
y = „ of adulterant.
z = „ of mixture.

$$a = \frac{100\,(x - z)}{x - y}.$$

From this equation we have for a in the two cases of admixture with rape oil above given the values 43·9 and 28·7 respectively, so that the experimental results are as good as could be expected in such a case.

It may be concluded that although refractometer analysis may be made to give fair results, with mixtures of known composition, it is not yet in a condition to give reliable results with the very complicated mixtures of unknown composition to which it might be applied.

H. Wolff investigated how the addition of rosin to boiled oil specially affected its normal refraction. He used Zeiss's butyro-refractometer at 15° and sodium light. By using six different sorts of linseed oil, and five sorts of rosin, he himself made a very large series of boiled oil in his laboratory and tested them with the following results:—

TABLE SHOWING EFFECT OF THE PRESENCE IN SOLUTION OF DIFFERENT PERCENTAGES OF ROSIN ON THE INDEX OF REFRACTION OF BOILED LINSEED OIL.

	Lowest Butyrometer Degree.	Average Butyrometer Degree.	Maximum Butyrometer Degree.
20 rosin-free boiled oils	86·2	88·0	91·2
12 boiled oils with 3 per cent. rosin .	88·5	90·0	92·2
12 ,, ,, ,, 5 ,, ,, .	91·8	92·5	94·0
15 ,, ,, ,, 10 ,, ,, .	96·7	97·5	100·0
	Index of Refraction	Index of Refraction	Index of Refraction
10 ,, ,, ,, 15 ,, ,, .	1·4896	1·4920	1·4975
5 ,, ,, ,, 20 ,, ,, .	1·4960	1·4980	1·5012

With boiled oils containing more than 10 per cent. of rosin, the whole field of view is illuminated. The boiled oil is then diluted with an equal weight of turpentine oil of known refraction and the mixture tested. If the index of refraction found be ng and that of the turps nt then the index of the boiled oil to be determined is

$$x = 2{\cdot}09\ ng - 1{\cdot}093\ nt + 0{\cdot}003,$$

Wolff asserts that in all boiled oils with a higher density and a refraction above 92, the rosin should be quantitatively estimated.

TABLE SHOWING THE INDEX OF REFRACTION OF DIFFERENT FRACTIONS OF RUSSIAN, ALSATIAN, GERMAN, AMERICAN, AND BAKU PETROLEUM. (ENGLER.)

Petroleum.	Fraction: 140°-160° C.		190°-210° C.		240°-260° C.		219°-310° C.	
	Density.	Index.	Density.	Index.	Density.	Index.	Density.	Index.
Tegernsee .	0·7465	1·427	0·7840	1·437	0·8130	1·451	0·8370	1·465
Pechelbronn .	0·7550	1·421	0·7900	1·440	0·8155	1·454	0·8320	1·462
Oelheim . .	0·7830	1·435	0·8155	1·450	0·8420	1·468	0·8625	1·480
Pennsylvanien	0·7550	1·422	0·7860	1·439	0·8120	1·454	0·8325	1·463
Baku . .	0·7820	1·436	0·8195	1·451	0·8445	1·467	0 8640	1·475

The above indices seem in some instances to overlap those of spirits of turpentine and of some drying oils.

TABLE SHOWING THAT NO CORRELATION EXISTS BETWEEN THE INDEX OF REFRACTION AND THE FIGURES EXPRESSING THE OXYGEN ABSORPTION PER CENT.

	Butyro-Refractometric Degree at 25° C.	Butyro-Refractometric Degree at 40° C.	Average Oxygen Absorption per Cent. Glass-plate Tests.
Linseed for varnish-making .	81·5	72·5	—
,, for paint purposes .	81·3	72·4	18·0
,, from Indian seed .	80·2	71·4	17·1
Paint linseed oil N. . .	80·8	—	—
Linseed oil W, three years old, not completely sealed .	82·2	—	15·4
Linseed oil of English origin, five years old, perfectly sealed	85·1	76·1	19·8

TABLE SHOWING FOR TREATED LINSEED OIL, THAT IS, REFINED RAW LINSEED OIL AND BOILED LINSEED OIL, THAT THERE IS NO CORRELATION BETWEEN THE INDEX OF REFRACTION AND THE FIGURES EXPRESSING THE OXYGEN ABSORPTION PER CENT. OF SUCH OILS.

	Butyro-Refractometric Degree at 25° C.	Butyro-Refractometric Degree at 25° C.	Average Oxygen Absorption per Cent. Glass Plate Tests.
Natural bleached, raw linseed oil (commercial) . . .	81·5	—	—
Paint oil A, Table 12, 11 months in beaker glass exposed to air	83·0	—	—
Paint oil A, treated with fullers' earth at 80° C.	81·5	72·5	—
Linseed oil, heated by superheated steam to 250° C. . . .	81·5	72·5	15·3
Varnish linseed oil, Table 4, heated for 1 minute to 250° C.	—	72·5	—
Paint oil A, heated for 6 hours at 150° C.	—	73·7	—
Paint oil N, heated in test tube to about 280° C., freed from mucilage	81·0	—	—
Paint oil A, heated in litre flask to 280° C., demucilaginated . .	82·1	—	16·5
Paint oil, heated in litre flask to 300° C.	82·5	—	—
Paint oil, heated for 40 hours to 180 to 190° C.	90·9	—	—
Paint oil, heated 5 minutes to 360° C.	102·3	—	5·43
Linseed oil W., Table 1, heated in bulk from 100 to 140 and air blown, kept 3 years and not absolutely hermetically sealed .	84·2	—	14·5
Cold blown linseed oil, 3 years old	83·4	—	—
,, ,, paint oil . . .	—	73·6	—
Paint oil A, warm blown . .	—	74·2	—
Cold blown from Indian linseed, Table 3	80·2	—	16·7
Hot blown from Indian linseed, 150° C., 20 hours . . .	92·6	—	—

Correlation of Index of Refraction and Iodine Absorption Per Cent.—In the same way the iodine absorption is connected with the index of refraction as shown in table.

TABLE SHOWING CORRELATION OF IODINE ABSORPTION PER CENT. OF LINSEED OIL WITH ITS INDEX OF REFRACTION. (THOMSON AND DUNLOP.)

Source.	Iodine No. (Wijs).	Butyro-Refractometer Degree at 25° C.	= Index of Refraction.
Riga	205·4	85·5	
Petrograd	200·0	84·2	
North America	194·6	83·2	
Calcutta	188·6	81·7	
La Plata	185·5	81·0	

But this parallelism, this simultaneous decrease of both factors can only apply to freshly expressed raw oil from fresh seed.

POLARIMETRIC TESTS.

The researches of Bishop and Peters on the opticity of a number of oils show that with the exception of castor oil, croton oil, and rosin oil, only dextro rotations are produced by sesame (high) and olive oil (feeble), all the others, including linseed oil, being either optically inactive or having a slight lævo-rotatory power.

1. *The Polarimetric Examination of Linseed Oil Sophisticated with Refined Rosin Oil (R.R.O.).*—According to Aignan such a mixture rotates the plane of polarisation to the right by an angle perceptibly proportional to the quantity of rosin oil which it contains. If the rotation observed with a 200 millimetre tube be represented by $[a]_D$ and the weight of the rosin oil in 100 parts by weight of the mixture by h, we get in the case of a mixture of linseed oil with—

1. Refined rosin oil $[a]_D = + \frac{14}{15} h$.
2. Choice white rosin oil $[a]_D = + \frac{17}{15} h$.
3. Rectified rosin oil $[a]_D = + \frac{21}{15} h$.

The first mixture is the most common. In actual practice, therefore, all that has to be done is to measure $[a]_D$ by the polarimeter, and to estimate h as refined rosin oil, according to the formula $h = [a]_D \frac{15}{14}$. The oils in question being dark in colour, it is better to work in a 100 millimetre tube and to calculate

$$h = [a]_D = \frac{15}{7}.$$

2. *Estimation of Rosin Oil in Paint by the Polarimeter.*—(*a*) A certain amount of the paint is frequently stirred and shaken up with ether and allowed to settle. The ether containing the oil in solution floats to the surface and the polarisation tube is filled with the ethereal

solution. If no optical deviation be produced, there is no rosin oil in the paint tested. On the other hand, if $[a]_D$ be the rotation towards the right with a 200 millimetre tube, according to Aignan's researches on the rotatory power of an ethereal solution of linseed oil containing rosin oil, the proportion of rosin oil may be calculated by the formula—

$$h = \frac{a[_D]}{43^2}.$$

(*b*) A known weight p^1 of the ethereal solution is run into a flask and heated on the water-bath at 100° C. (212° F.) so as to drive off the ether; the oil which boils only at 300° C. (572° F.) is left in the flask. Let its weight be represented by p^2. The proportion $\frac{p^1}{p^2} 100 = h^1$ per cent. of oil (linseed oil and rosin oil) contained in the ethereal solution examined by the polarimeter. If $h^1 = h$, it may be taken for granted that the paint contained linseed oil free from rosin oil. Generally h^1 is greater than h, then $\frac{h}{h^1} 100$ will give the percentage of rosin oil contained in the linseed oil which was used to make the paint.

THE ROTATORY POWER EXERTED ON THE PLANE OF POLARISATION BY VARIOUS OILS ACCORDING TO DIFFERENT OBSERVERS.

Oils.	Authorities.			
	Bishop.	Peters.	Toxier.	Girard.
Arachis . . .	-0·4	-2·1 to +0·5	0 to + 0·1	- 0·3
Beech . . .	—	—	- 1	- 0·8
Camelina. . .	—	—	0·7	- 2·3
Castor . . .	—	40·7	+ 38·5 to - 48	+ 43
Colza . French,	-2·1	-0·53 to -1·3	- 1·3 to - 2^{1}	- 0·8
Japan	-1·6			
Cotton . . .	—	-0·7	- 1·3	- 1
Croton . . .	—	+42·5	—	+ 46
Hemp-seed . .	—	—	- 0·7	- 0·5
Linseed . . .	-0·3	-0·3	- 0·7 to 0·4	—
Maize . . .	—	—	- 1·3	—
Olive . . .	+0·6	+0·4 to 1	Lubricating +1·0to1·3 Burning + 1·0 Edible + 0·7	+ 0·5
Poppy . . .	0	-0·1 to -0·7	- 0·3 to - 0·5	—
Rape . . .	—	—	- 1·3	+ 1·0
Sesame old	+3·1	+5	+ 5 to + 5·1	+ 5
hot pressed	+7·2			
1878	+4·6			
1882	+3·9			
India 1884	+7·7			
Stillingia . .	—	—	—	—
Walnut . . .	-0·3	-0·3	- 0·7 to - 0·4	-6·45° in 20 mm. tube='+29 Sacch. °
Wood . . .	—	—	0	—

OPTICAL DEVIATION OF ROSIN OIL AND MINERAL OILS.

	Rosin Oils.	Mineral Oils.
D = 1000	+ 51·7	Russian D = 0·906 to 0·908 + 15·6 to + 19
9685	+ 44·4	American D = 0·883 to 0·910, 0 to + 2
9849	+ 41·2	Russian Valvolines D = 0·914 + 22·4 to + 26·5
9768	- 38·7	American Valvolines D = 0 882 to 0·890, 0 to + 0·8
9805	+ 36·0	—
9854	- 30·7	—
9898	+ 26·0	—

CHAPTER IX.

THE ADULTERATION OF LINSEED OIL.

Oil Crushing. Hot and Cold Pressed Linseed.—Ketel and Antusch found iodine values under 106 in oil extracted from powdered linseed-oil cake. Microscopic examination showed that the original seed had contained less than 10 per cent. of foreign seed. The extracted fatty matter was not rancid, but white, solid, and granular, and in several instances gave, with alcoholic silver nitrate, a decided reaction characteristic of cotton-seed oil. Van Ketel and Antusch concluded that the oilcake contained an addition of foreign fat. Mastbaum did not agree with this conclusion, arguing that during pressing a flow of different glycerides may take place, and that the lighter fluids would be the first to leave the press. Faszbender and Kern have shown that this actually takes place. Five kilogrammes of linseed with 9 per cent. of foreign seed, of which 5·3 per cent. was cruciferous seed, were divided into two portions, of which one portion was prepared, the other not. Then both were pressed first in the cold, then hot pressed, then extracted with petroleum ether and then the iodine values of the oils determined. The extracted oil amounted to 37 per cent.

TABLE SHOWING VARIATIONS IN ANALYTICAL RESULTS OF COLD AND HOT PRESSED LINSEED OILS.

	Prepared.	Unprepared.	Oil Content of Residue.
I. Cold pressed	180·3	180·5	25 per cent.
II. Pressed at 70° C.. . . .	180·3	175·3	12 „
III. Extracted by petroleum ether .	179·9	162·5	—

The first point in connection with the impurities in linseed oil is that of their origin, viz. one class of impurities is due to the contamination of the oil seeds with other seeds. If these foreign seeds be oil-free seeds they have little effect on (*a*) the yield of oil, or (*b*) its quality. Their effect is negative, but if they be oleiferous then their oil content is mixed with that from the linseed and affects the chemical composition of the linseed oil crushed from such impure seed. Accord-to Wijs (1) Dutch seed contains little foreign seed; (2) La Plata seed has most; 5 per cent. at least, but almost exclusively oil-free seed. Again (3) British-Indian linseed rarely exceeds 6 per cent. of foreign seed, and these are mostly oil-free, but occasionally 1 per cent. of brassica (rape-seeds). There comes from (4) Calcutta, a very inferior grade of linseed which is said to be shipped with as much as 20 per cent. of foreign oleiferous seeds; (5) South Russian Black Sea seed is apparently pure, but it mostly contains brassica seeds. Again (6) North Russian Baltic seed is impure—5 per cent. is little of foreign seeds, 10 to 20 per cent. is often present, and if higher constants be found only brassica and camelina seeds are present; (7) North American seed is apparently always pure, and such foreign seeds as are present are seldom oleiferous. Faszbender and Kern found seed to contain up to 10 per cent. of foreign seed, chiefly cruciferous, such as rape, brassica, hedge mustard, raphanus, mustard sinapis. According to the specification of the Incorporated Oil Seed Association of London, good linseed should not contain more than 4 per cent. of foreign seed. The manner in which the oil from the above-known seeds affects the known constants of linseed oil is shown in the following table.

TABLE SHOWING THE IODINE VALUE OF (*a*) LINSEED OIL; (*b*) OF THE OILS FROM THE FOREIGN SEEDS WITH WHICH IT IS LIABLE TO BE MIXED. THE FIGURES ARE THOSE OF KETEL AND ANTUSCH. THE OILS ARE EXTRACTED BY PETROL-ETHER.

Oils from—	Iodine Value of the Oil.
Pure linseed	181-187
,, camelina seed	146
,, colza seed	101
90 per cent. linseed + 10 camelina	179
85 ,, ,, + 15 ,,	172
80 ,, ,, + 20 ,,	170
90 ,, ,, + 10 colza	173
85 ,, ,, + 4 camelina + 11 colza	174
90 ,, ,, + 3 ,, + 4 ,,	176

Foreign seeds in linseed, therefore, alter the composition of the linseed oil extracted therefrom in the same way as when other oils are added to it. Of the four oils here given (1) hedge mustard oil, raphanus, is not crushed for oil; (2) mustard seed is, as a rule, dearer than linseed; (3) camelina oil is seldom met with; and (4) rape. In Belgium, Holland, the Balkan States, and Russia the plants are extensively cultivated, and L. E. Andés asserts that linseed oil can be mixed with its own weight of camelina seed without affecting its drying properties. But it has already been pointed out that in linseed oil-crushing other points require attention besides the suitability of the oil for its intended use. Now the oil from camelina sativa leaves a residual cake which is too acrid for cattle ("Gardener's Chronicle," 1843, p. 678). If therefore the oil crusher receives a cargo of linseed containing camelina seed, he is running a great risk of having all the oil cake from it thrown on his hands if he accepts delivery. The crusher must bear in mind that the agricultural chemist applies two organoleptic tests to linseed cake, and it is a *sine qua non* they should pass both taste and smell. A linseed-oil cake acrid from camelina, or other cruciferous seed, e.g. rape, will most certainly be condemned. If oil chemists, pure and simple, gloss over such points the crusher cannot. Besides oil containing cruciferous oils are liable to darken when used as a vehicle for white lead.

TABLE SHOWING THE CHEMICAL AND PHYSICAL CONSTANTS OF LINSEED OIL, CAMELINA OIL, RAPE OIL, MUSTARD OIL, HEDGE MUSTARD OIL.

	Linseed Oil.	Camelina Oil.	Rape Oil.	Mustard-seed Oil.	Hedge Mustard Oil.
$d\frac{15}{15}$	0·930-0·936	0·923-0·927	0·913-0·917	0·916-0·920	0·9175
Solidification-point .	−8 to 20° C.	−18 to 19° C.	0 to −6° C.	−17·5° C.	Below 0·8° C.
Index of refraction .	80-85	—	67°-69·2	69	—
Acid number . .	Up to 6	—	Up to 4	Up to 3	—
Saponification number	189-195	185-188	167-179	174-182	174
Iodine number . .	170-200	135-153	94-106	103-122	105
Unsaponifiable . .	Up to 2%	—	1·0-1·5%	—	—
Melting-point of fatty acids . . .	17-21°	18-20°	16-22°	15-17°	—
Solidification-point of fatty acids . .	13-17°	13-18°	12-18°	15·5°	—

It will be seen that all four oils lower the density, saponification number and iodine number.

Rape Oil.—Adulteration with rape oil occurs when the addition of as little as 10 per cent. s profitable owing to the high price of linseed oil. Such an addition would affect the constants of linseed oil. Rape oil contains an unsaturated fatty acid, characteristic of the fatty acids of all cruciferous oils, erucic acid, $C_{22}H_{42}O_2$, which limits the high molecular weight and the lower saponification value of rape oil. Erucic acid is differentiated from the homologue of oleic acid by its high m.p., 34° C., also by the difficulty with which its lead salt dissolves in ether.

Detection of Rape and other Oils in Linseed Oil.—The easiest, quickest, and best way to detect colza oil (commercial) or ordinary rape oil is by the elaiden test, which blackens in contact therewith. During an experience of many years the author never came across a sample of commercial colza or rape oil that did not respond to this test by blackening. Holde and Marcusson's method.—From 20 to 25 grammes of the fatty acids of the oil to be tested are mixed with double their volume of 96 per cent. alcohol, and the solution cooled, in a wide test tube whilst stirring with a glass rod, and by the aid of a freezing mixture, to − 20° C. A precipitate occurs which consists chiefly of the saturated fatty acids of linseed oil, myristic, and palmitic acids. It is drained in a cold funnel at − 20° C. and washed with cooled alcohol. The filtrate is evaporated, the residue dissolved in four times its volume of 75 per cent. alcohol, and the solution cooled to − 20° C. If rape oil be present, after a lapse of an hour a crystalline precipitate of erucic acid occurs. It is drained and washed with 75 per cent. alcohol. It then appears pure white, but besides erucic acid it contains other acids, the removal of which is not necessary. The acid mixture is dissolved in much ether or benzol, the filtered solution evaporated, and (1) the melting-point, (2) acid value, and (3) molecular weight determined. The melting-point is under 30° C., the molecular weight between 310 and 320, and the iodine number about 60, erucic acid 75·1, of the other vegetable oils known to be used as linseed oil adulterants; the principal ones are, (1) cotton-seed oil, (2) maize oil, and (3) soya-bean oil. (1) Cotton-seed oil is derived from the seeds of the cotton plant, and produced since the sixties of last century in large quantities, chiefly in the U.S.A., and after suitable refining brought on to the markets of the world; (2) maize oil is another U.S.A. product, extracted from the germ of the seed of zea mais. In the U.S.A. its manufacture has, of late years, become very important; (3) the soya bean is the product of a shrubby plant, up to now almost exclusively cultivated in Manchuria. It first appeared on the world's markets a few years ago. The first cargo was landed in Germany in 1910. All three oils are pale yellow in colour, and when refined almost without taste and smell. Their constants are given in the following table, with those of linseed oil in parallel column for better contrast.

TABLE SHOWING THE CHEMICAL AND PHYSICAL CONSTANTS OF LINSEED, COTTON-SEED, MAIZE, AND BEAN OILS.

	Linseed Oil.	Cotton-seed Oil.	Maize Oil.	Chinese Bean Oil (Soya).
Specific gravity at 15° C.	0·930-0·936	0·922-0·930	0·921-0·924	0·924-0·929
Solidification-point .	− 8 to − 20°C.	− 1 to + 4°C.	− 10 to − 15° C.	− 14 to − 15° C.
Butyro-refractomer Degree . . .	80-85	67-75	77·5	—
Equal to an index of refraction of acid number . . .	Up to 6	1	—	Up to 5
Saponification number	189-195	191-198	188-193	190-193
Iodine number . .	170-200	101-117	111-130	121-137
Hexabromide number.	22-37	0	0	1·2-2·9
Unsaponifiable . .	Up to 2 °/o	0·7 to 1·7 °/o	1·3 to 1·6 °/o	0·2
Melting-point of the fatty acids . .	17-21° C.	34-43° C.	16-23° C.	26-29° C.
Solidifying-point of the fatty acids . .	13-17° C.	28-36° C.	13-16° C.	23-25° C.

The high melting-point of cotton-seed oil fatty acids, with their wide range of melting-points, is characteristic. It also comes on the market as stearine-free cotton-seed oil, which during prolonged storage in the cold has deposited a large amount of its solid glycerides. For the special detection of cotton-seed oil many different colour reactions are given, but none of them are free from objection, at least none such as are to be found in the literature. The silver nitrate test, according to Milian, is applied thus: Five c.c. of the mixed fatty acids are dissolved in 15 c.c. of 90 per cent. alcohol, the solution heated to incipient ebullition, then 2 c.c. of silver nitrate solution, 30 grammes in 100 c.c. of water, added. Two per cent. of cotton-seed oil gives a characteristic brown colour.

In Halphen's reaction a 1 per cent. solution of sulphur, in carbon disulphide, acts as the reagent. Equal volumes of amyl alcohol and the above solution are shaken in a test tube (for $\frac{1}{4}$ to $\frac{1}{2}$ hour), placed in a boiling solution of common salt, the CS_2 is evaporated to about 5 per cent., when the cotton-seed oil assumes an orange-red to red coloration.

Soya-bean oil as a new comer has been little studied. Its "constants," to some extent, approach those of linseed oil, so that small quantities in linseed oil would be difficult to detect. Meister found it so. Meister regards soya-bean oil as a fair drying oil. But it has several drawbacks. It bleaches better than linseed oil but darkens more on heating with driers. Moreover, the oil skin or coat obtained from bean oil is softer and more easily abraded. Finally, bean oil and the boiled oil derived from it exhibit peculiar properties. It does not dry out to a uniform film like linseed oil but generally in irregular flakes and streaks which dry lustrous, whilst the smooth paint dries flat. Apparently it can only be used in admixture. Meister limits the amount of bean oil that can be added to linseed oil to 25 or 35 per cent. at the most.

Linseed Oil Sophisticated with Maize Oil.—As to maize oil its detection is much more delicate; a colour reaction has been given for its detection in linseed oil, but it has not been confirmed. If the addition of concentrated sulphuric acid gives a characteristic grey colour lasting for a minute, then the solution of the oil in carbon disulphide gives a violet colour with a drop of concentrated sulphuric within 24 hours. Moreover, maize oil contains sitosterin instead of the usual phytosterin of m.p. 137·5 to 138, and this fact is utilised in its detection.

The iodine number of maize oil is too high, altogether abnormal, thus differing from the iodine number of number 2 and the iodine numbers of different authorities: 123·3 to 124·6 Tortelli and Ruggieri, 116·3 Smetham, 130·8 Lewkowitsch, 122·7 Archbutt. Cotton-seed oil will lower the percentage of liquid fatty acids in linseed oil to a far greater extent than maize oil or any other vegetable oil.

Linseed Oil Sophisticated with Fish Oils.—Several fish oils are added to linseed oil. Their usually high iodine number favours the

TABLE OF COMPARISON OF PHYSICAL AND CHEMICAL DATA OF TWO POSSIBLE ADULTERANTS OF LINSEED OIL, VIZ. COTTON-SEED OIL AND MAIZE OIL.

	Butyro-Refractometer Degrees at 25° C.	Saponification Number.	Iodine Number.	Acetyl Number.	Iodine Number of Fatty Acids.	Maumené Test Degrees C.	Melting-point of Fatty Acids.
Cotton oils:—							
Cotton planters	68	194·07	107·15	19·49	112·5	63·5	36 to 37
Aldigo . .	67·25	194·87	104·75	20·06	111·5	63	"
Delmonus .	67·25	200·4	106·62	28·04	113·2	66·5	"
Cotton-park .	68·28	194·45	107·1	19·28	113·06	58	"
Maize oil 1 . .	71·25	188·11	147·60	20·58	151·40	73·5	18 to 20
" " 2 . .	70	180·82	124·50	22·75	130·20	72	"

adulteration. The chief adulterants are (1) commercial cod oil (the medicinal oil is too dear), (2) sardine oil, and (3) more especially in U.S.A., menhaden oil. Cod oil comes from Newfoundland, Norway, and the East Coast of Great Britain, the oil is sometimes allowed to exude from the livers spontaneously, or it is expressed. Sardine fish oil, from the Spanish coast, is obtained from a well-known small fish. In the literature its composition is mixed up with Japanese fish oils, but that is not correct. The Spanish sardine oil has the highest iodine number of any fish oil, whereas most Japanese fish oils have very low iodine numbers. Menhaden oil is obtained on the coast of North America, from a fish allied to the herring (? mackerel). Figures for fish oils vary greatly, partly owing to the condition in which they are marketed, through freeing the oil by cooling from a portion of its solid glycerides, fish tallow and such oils differ to the extent and manner in which the crude oil has been freed from solid fat. J. Hertkorn tried by extreme cooling under specially elaborate conditions to force the oil to deposit its solid fat and to use the thin fluid oil so obtained as a linseed oil substitute.

TABLE SHOWING THE CHEMICAL AND PHYSICAL CONSTANTS OF LINSEED OIL, COD OIL, SARDINE OIL, AND MENHADEN OIL.

	Linseed Oil.	Cod Oil.	Sardine Oil.	Menhaden Oil.
Specific gravity at 15° C.	0·930-0·936	0·920-0·930	0·928-0·934	0·925-0·933
Solidification-point .	- 8 to - 20° C.	Mostly over 0°	Mostly over 0°	—
Butyro-refractometric degree . . .	80-85	80-85	—	80-83
Equal to an index of refraction of acid number	Up to 6	Up to 25	Up to 20	Up to 15
Saponification number .	189-195	182-187	188-194	188-193
Iodine number . .	170-200	150-170	170-200	145-175
Hexabromide number .	22-37	33-43	—	—
Unsaponifiable . .	Up to 2	Up to 2	Up to 2	Up to 2·2

The characteristic smell of fish oil is the chief method of detecting it. But almost odourless sorts are on the market. The smell of the original fish oil, however, reappears when the deodorised oil is warmed by rubbing between the palms of the hands. Bearn, on treating a suspected oil with steam and collecting the distillate, found an unmistakable fish smell. Even 2 per cent. of fish oil can be so detected. A whole series of colour reactions are given for the detection of fish oil, but none are reliable. On the other hand, the unsaponifiable should lend itself without objection to the detection of fish oil, but up to now no such research has succeeded. Lippert separated the unsaponifiable from a fish oil and examined it closely. He obtained a thick unpleasant-smelling oil readily soluble in acetic acid, like rosin oil; the solution gave with acetic acid a bright red colour. Later he isolated cetyl alcohol from the unsaponifiable with a m.p. of 50° C. Up to now that alcohol has only been identified with certainty in walrus oil. Cholesterin occurs in ordinary fish oil. It has been already shown that linseed oil unsaponifiable on three crystallisations from absolute alcohol yields phytosterin crystals of m.p. 137·5 to 138° C. Fish oil does not seem to be capable of detection in this way nor by the so-called phytosterin acetate test. In that test the unsaponifiable from 100 grammes of oil and 2 to 3 grammes of acetic anhydride are heated to boiling for ½ hour in a small porcelain basin, covered with a watch glass and the excess evaporated on the water-bath. The resulting acetyl-ester is as often as possible crystallised from absolute alcohol and its melting-point determined. Phytosterin acetate from linseed oil melts at 128 to 129° C. The cholesterin acetate from pig's fat melts at 113·6° C. H. Bull separated highly unsaturated fatty acids from fish oil, their sodium salts being soluble in a little absolute alcohol containing ether. He believed such fatty acids may be used to detect fish oil in linseed oil. On the other hand, Frujimoto isolated from various fish oils an unsaturated fatty acid with four double bonds, clupadonic acid, $C_{18}H_{28}O_2$, and in the form of its octobromide, $C_{18}H_{28}Br_8O_2$, insoluble in ether. This octobromide is differentiated from hexabromlinolenic acid, of m.p. 175 to 180° C., by the fact that it blackens at 200° C. By aid of this property 10 per cent. of fish oil can be detected in linseed oil.

Adulteration of Raw Linseed Oil.—Amongst other adulterants than glycerides, mineral oil, rosin oil, and rosin occur, whilst the first-named oil, linseed oil, still remains so cheap that even slight adulteration therewith is profitable. Rosin was formerly cheap, as low as 2s. 6d. per cwt., and in those days rosin oil was the classical—the one and only—adulterant, but in the last three decades rosin has risen in price twelvefold or more and now rivals some of the cheaper copals.

TABLE SHOWING CHEMICAL AND PHYSICAL CONSTANTS OF LINSEED, MINERAL AND ROSIN OILS, ALSO ROSIN.

	Linseed Oil.	Mineral Oil.	Rosin Oil.	Rosin.
Specific gravity at 15° C.	0·930-0·936	0·8-0·920	0·96-0·990	About 1·1
Refraction at 15° C. .	1·484-1·488	1·439-1·508	1·536-1·550	1·548
Acid number . . .	Up to 6	0	Up to 50	140-180
Saponification number .	189-195	Up to 3	Up to 65	160-190
Iodine number . .	170-200	Up to 14	45-48	140-180
Unsaponifiable . .	Up to 2 p.c.	97-100 p.c.	70-90 p.c.	Up to 15 p.c.

Mineral Oil as an Adulterant of Raw Linseed Oil.—Mineral oil used to reduce linseed oil consists of a certain fraction from crude petroleum or certain fractions of shale oil distillates—fractions which are exclusively unsaponifiable hydrocarbides. Its acid number is therefore 0, although some sorts contain traces of sulphuric acid from the refining. The saponification number should likewise be 0, although, as a rule, on treatment with alcoholic potash, 1 or 2 per cent. is absorbed. The saponification number and the iodine number of linseed oil are necessarily lowered by mineral oil, whilst the percentage of unsaponifiable is increased. Qualitatively the presence of mineral oil in linseed oil in not too small a quantity is detected by the so-called water reaction. One gramme of the suspected oil is heated in a test tube, with constant shaking, with 5 c.c. double normal alcoholic potash. Pure linseed oil gives, after a few minutes, a clear soap solution, which remains clear on the addition of water. Linseed oil, containing mineral oil, does not give a clear solution, even on long boiling, and on the addition of water turbidity persists. The insoluble mineral oil separates out on long standing. With a small amount of mineral oil the alcohol solution may remain clear, but on adding water it becomes cloudy. Thoms and Fendur have shown that pure linseed oil contains less than 2 per cent. of a homogeneous wax-like mass, completely soluble in warm alcohol, with an iodine number of 80 to 90. On the other hand, the unsaponifiable in the presence of mineral oil is in greater part fluid, from which phytosterin crystals separate out on heating with 90 per cent. alcohol. Small drops remain undissolved. The weight is more than 2 per cent. and the iodine number below 80. In a special case a linseed oil gave 2·86 per cent. unsaponifiable, with an iodine number of 38·2. A pure linseed oil was mixed with 2 per cent. mineral oil, and on analysis the percentage of unsaponifiable had risen from 1·05 to 2·82, and the iodine number fallen from 83·9 to 35 per cent. Therefore the opinion that the suspected oil contained 2 per cent. mineral oil was confirmed. It is to be remarked that such a small percentage need not necessarily imply adulteration, as the hydraulic presses in oil mills instead of water are often sprinkled with mineral oil, from which a small quantity may pass into the expressed oil. Again it is possible during the analysis for light mineral oil on prolonged heating to 90 to 100° C. to lose at most a per cent. or two of its weight.

Rosin Oil as an Adulterant of Raw Linseed Oil.—Rosin oil is produced by the dry distillation of rosin; it consists mostly of hydrocarbides, but it may also contain a certain content of rosin acids and anhydro-derivatives of the same. It does not therefore lower the iodine number nor the saponification number of linseed oil to such an extent as mineral oil. On the other hand, it increases the specific gravity and the degree of refraction, but more especially the optical deviation, which of linseed oil is practically nil, but is increased up to 50° in the presence of rosin oil. Argnan first used this test for the detection of rosin oil in linseed oil. Mineral oil differs from rosin oil by its high iodine number and by its greater solubility in alcohol, therefore greater quantities are required for the water reaction. Finally rosin oil withstands the action of nitric acid to a much less extent than mineral oil. If a mixture of both be heated with nitric acid of specific gravity 1·2, diluted with water and shaken up with ether, almost all the mineral oil is separated. The Storch-Morawski test[1] applies not only to rosin oil but to the mother substance, rosin itself. One to three drops of oil to be tested are heated to boiling in a test tube with 2 to 3 c.c. acetic anhydride. On complete cooling one drop of concentrated H_2SO_4 is added without running down the inner side of the tube. On gentle shaking a beautiful violet fugitive coloration is produced.

Source of Rosin.—Rosin remains as a residue when turps is distilled from turpentine-oleo-resin. It consists chiefly of abietic acid, $C_{20}H_{30}O_2$, an unsaturated cyclic acid with two double bonds but containing a small quantity of hydrocarbides. Dissolved in linseed oil it increases the viscosity (consistency-body), the specific gravity, and the acid number. On the other hand, the saponification number and the iodine number, as well as the unsaponifiable, are not influenced to a very appreciable extent. The index of refraction, as with rosin oil, rises, e.g. R. Schinck found the refraction of a linseed oil at 40° C. to be 71·5 butyro-refractometric degrees; the same oil with 20 per cent. rosin from various sources gave 90·7 to 92·3°. Under the water reaction rosin behaves normally. For the detection of small quantities of rosin the suspected sample of linseed oil is treated with 80 per cent. alcohol; rosin when present in quantity will be found in the evaporated residue. Abietic acid is distinguished from fatty acids by the fact that on leading gaseous HCl into the alcoholic solution, it is not etherified. Twitchell has accordingly based a method for the quantitative estimation of rosin. This method has been made handier by H. Wolff. The estimation of rosin, in a rosin fatty acid mixture, is determined thus: 100 c.c. alcohol (95 per cent., or absolute) are at summer temperature mixed with 20 to 25 c.c. concentrated H_2SO_4, and 0·5 gramme ground potassium bisulphate. Five grammes of the fatty acid mixture to be tested are dissolved in 15 c.c. absolute alcohol and the solution heated with 30 c.c. of the above alcoholic H_2SO_4, etc., for 10 to 15 minutes, in a *reflux* condenser. From 400 to 500 c.c. of water are added through the condenser tube, and the fluid shaken with a mixture of ether and petroleum ether. The extract is washed three times with water, then mixed with 4 parts of alcohol, and neutralised with ½ normal soda NaOH. The result is calculated to abietic acid, the molecular weight 350 being adopted. As a control, the rosin acids may be estimated by the gravimetric method.

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[1] This test is better known as the Liebermann-Storch reaction. The reader will notice that the test has been previously referred to by the author for some reason or other as the Storch-Morawski test.

Effect of Adulterants on the Drying of Raw Linseed Oil.—Linseed oil is the drying oil *par excellence*, if we know *a priori* that all adulterants and doctored products impede its drying. The oxygen absorption is in that case lowered. The falsification of linseed oil by other oils prevails to some extent, especially when it attains an abnormal market figure. Well-known semi-drying oils are used as linseed oil substitutes, resulting in the drying process of linseed oil being affected. In two special researches soya-bean oil and different fish oils have been found.

The following results were obtained by comparative tests with linseed oil and bean oil. also mixtures:—

EFFECT OF ADULTERATION WITH SOYA-BEAN OIL ON DRYING AND WEIGHT OF OXYGEN ABSORBED PER CENT. COMPARED WITH LINSEED OIL.

	Time of Drying, Hours.	Oxygen Absorption, Per Cent.
Linseed oil, raw	78	19·5
Bean oil, raw	144	16·9
Linseed oil bleached by fuller's earth	72	20·7
Bean oil	120	10·1
Linseed oil 1 hour heated to 250° C.	72	18·7
Bean oil 1 hour heated to 250° C.	114	18·3
75 parts B., 25 parts L., raw	138	17·3
50 „ „ 50 „ „ „	114	15·7
25 „ „ 75 „ „ „	114	15·0
Linseed oil with 2 per cent. manganese rosinate	8	17·9
Bean oil with 2 per cent. manganese rosinate	13	18·7
Linseed oil with 2 per cent. lead rosinate	36	17·2
Bean oil with 2 per cent. lead rosinate	52	16·4
Linseed oil with 2 per cent. lead manganese rosinate	7	18·1
Bean oil with 2 per cent. lead manganese rosinate	13	15·4
75 parts L., 25 parts B., 2 per cent. mn. rosinate	14	14·1
75 „ „ 25 „ „ 5 „ pb. mn. rosinate	8	4·1

OXYGEN ABSORPTION PER HOUR OF: (1) RAW LINSEED OIL. (2 RAW SARDINE OIL. (3) BOILED LINSEED OIL. (4) BOILED SARDINE OIL; AND (5) A MIXTURE OF 75 PER CENT. LINSEED OIL AND 25 PER CENT. SARDINE OIL. (MEISTER.)

Hours.	Linseed Oil.	Sardine Oil.	Boiled Linseed Oil.	Boiled Sardine Oil.	Boiled Oil: 75 per Cent. Linseed. 25 per Cent. Sardine.
1	—	3·8	—	—	—
2	0·1	7·2	—	12·1	—
3	0·3	10·1	5·7	17·2	10·9
6	0·5	14·1	12·2	19·7	13·5
8	—	15·8	—	—	15·5
9	0·5	16·7	14·8	—	15·6
10	—	—	—	19·8	—
11	—	17·9	—	—	—
12	0·7	—	—	19·8	15·9
22	—	19·9	—	17·7	—
24	4·2	—	16·3	—	—
28	—	18·3	—	—	—
30	—	—	14·2	—	—
48	9·8	18·9	12·4	15·6	15·1
54	10·2	—	—	—	—
72	16·8	16·1	12·2	14·7	—
75	19·2	15·6	—	—	13·1
96	—	16·4	—	—	—
120	19·0	16·2	12·3	15·2	12·9
144	18·7	16·1	12·2	14·9	—
168	—	15·9	—	14·2	—
200	—	15·6	12·0	13·8	12·7

U.S.A. STANDARDS FOR RAW LINSEED OIL.

	1.	2.	3.	4.
Specific gravity at 15·5° C.	0·9345	0·9329	0·9333	0·9342
„ „ at 25° C.	0·9299	0·9284	0·9285	0·9295
Turbidity and foots	0·78 c.c.	0·35	0·40	0·65
Moisture and volatile matter				
(*a*)	0·056 per cent.	0·082	0·171	0·051
(*b*)	0·041 „	0·078	0·191	0 044
Ash	0·136 „	0·024	0·038	0·156
Acid number in MgsKOH	1·11	0·335	1·79	1·54
Saponification number	190·76	190·5	192·2	190·4
Unsaponifiable matter	1·00	0·956	[illegible]72	1·01
Refractive index	1·4798	1·4795	1·4797	1·4797
Iodine number	186·36	183·9	186·37	185·1

TABLE BY MEISTER SHOWING HOW LINSEED OILS, THE FIGURES OF WHICH ARE OTHERWISE NORMAL, MAY SHOW LOW IODINE NUMBERS.

Source of Oil.	Calcutta Seed.	La Plata Seed.	La Plata Seed.	1.	II.	III.	IV.
1. Butyro-refractometric degree[1] .	—	—	—	88	87	87	86·5
2. Specific gravity[1]	0·931	0·932	0·932	0·932	0 9305	0·9315	0·9310
3. Acid number	3·1	2·7	2·9	1·8	1·6	2·0	2·5
4. Saponification number . .	194·5	193·2	190·4	191·5	193·5	192·0	194·3
5. Iodine number	164·5	161·1	160·2	164	166	161	157
6. Unsaponifiable, per cent. .	1·5	1·7	1·2	—	—	—	—
7. Hexabromides ,, . .	25·2	24 1	22·3	25·8	33·9	27·3	32·0
8. Time of drying, hours . .	80	85	83	—	—	—	—
9. ,, ,, ,, at 18° . . .	—	—	—	80	85	85	90
10. Oxygen absorption, per cent. .	18·0	19·1	18·4	—	—	—	—
Fatty Acids—							
11. Specific gravity . .	—	—	—	0·923°	0·928	0·927	0·925
12. Solidification-point . .	—	—	—	13·5°	13·6°	13·5°	13·8°
13. Melting-point . . .	—	—	—	18·5-20°	20-21°	20·21°	21-22·5°

[1] Note how the butyro-refractometer degree in samples 1, 2, 3, 4 decreases as the specific gravity lowers.

OXYGEN ABSORPTION PER HOUR OF: (1) RAW LINSEED OIL. (2 RAW SARDINE OIL. (3) BOILED LINSEED OIL. (4) BOILED SARDINE OIL; AND (5) A MIXTURE OF 75 PER CENT. LINSEED OIL AND 25 PER CENT. SARDINE OIL. (MEISTER.)

Hours.	Linseed Oil.	Sardine Oil.	Boiled Linseed Oil.	Boiled Sardine Oil.	Boiled Oil: 75 per Cent. Linseed. 25 per Cent. Sardine.
1	—	3·8	—	—	—
2	0·1	7·2	—	12·1	—
3	0·3	10·1	5·7	17·2	10·9
6	0·5	14·1	12·2	19·7	13·5
8	—	15·8	—	—	15·5
9	0·5	16·7	14·8	—	15·6
10	—	—	—	19·8	—
11	—	17·9	—	—	—
12	0·7	—	—	19·8	15·9
22	—	19·9	—	17·7	—
24	4·2	—	16·3	—	—
28	—	18·3	—	—	—
30	—	—	14·2	—	—
48	9·8	18·9	12·4	15·6	15·1
54	10·2	—	—	—	—
72	16·8	16·1	12·2	14·7	—
75	19·2	15·6	—	—	13·1
96	—	16·4	—	—	—
120	19·0	16·2	12·3	15·2	12·9
144	18·7	16·1	12·2	14·9	—
168	—	15·9	—	14·2	—
200	—	15·6	12·0	13·8	12·7

U.S.A. STANDARDS FOR RAW LINSEED OIL.

	1.	2.	3.	4.
Specific gravity at 15·5° C.	0·9345	0·9329	0·9333	0·9342
" " at 25° C.	0·9299	0·9284	0·9285	0·9295
Turbidity and foots	0·78 c.c.	0·35	0·40	0·65
Moisture and volatile matter				
(a)	0·056 per cent.	0·082	0·171	0·051
(b)	0·041 "	0·078	0·191	0 044
Ash	0·136 "	0·024	0·038	0·156
Acid number in MgsKOH	1·11	0·335	1·79	1·54
Saponification number	190·76	190·5	192·2	190·4
Unsaponifiable matter	1·00	0·956	0·872	1·01
Refractive index	1·4798	1·4795	1·4797	1·4797
Iodine number	186·36	183·9	186·37	185·1

A raw linseed oil should be considered pure when it tests between the following:—

	Maximum.	Minimum.
Specific gravity at 15·5° C.	0·936	0·932
„ „ at 25° C.	0·931	0·9270
Acid number	6·00	—
Saponification number	192	189
Unsaponifiable matter	1·50 per cent.	—
Refractive index at 25° C.	1·4805	1·4790
Iodine number (Hanus)	190	178

Raw linseed oil from North American seed should conform to the following requirements:—

	Maximum.	Minimum.
Specific gravity at $\frac{15·5^\circ}{15·5^\circ}$ C.	0·936	0·932
or		
Specific gravity at $\frac{25^\circ}{25^\circ}$ C.	0·931	0·927
Acid number	6·00	—
Saponification number	195	189
Unsaponifiable matter, per cent.	1·50	—
Refractive index at 25° C.	1·4805	1·4790
Iodine number (Hanus)	—	180

Scheme for Examination of Linseed Oil for Purity or Otherwise.—(1) *Specific Gravity.*—Determine with a pyknometer or spindle at 15·6° C. (2) *Viscosity.*—Use the Engler method, making the determination at 20° C. (3) *Flash-point,* Open Cup.—Set a nickel crucible 60 mm. in diameter at the top, 40 mm. in diameter at the bottom, and 60 mm. in height in a hole in the middle of a sheet of asbestos board 200 mm. square. The bottom of the crucible should project about 25 mm. through the asbestos. Support the asbestos on a tripod and suspend a thermometer reading to 400° C. in degrees in the centre of the crucible, so that the lower end of the thermometer is 10 mm. from the bottom of the crucible. Then pour in the oil until its level is 15 mm. below the top of the crucible. Place a Bunsen burner below the crucible and regulate the size of flame so that the thermometer rises 9° a minute. As a test flame use an ordinary blow-pipe attached to a gas tube. The flame should be about 6 mm. long. Begin testing when the temperature of the oil reaches 220° C., and test for every rise of 3°. In applying the test move the flame slowly across the entire width of the crucible immediately in front of the thermometer, and 10 mm. above the surface of the oil. The flash-point is the lowest temperature at which the vapours above the oil flash and go out. (4) *Fire-point.*—After noting the temperature at which the oil flashes continue the heating until the vapours catch fire and burn over the surface of the oil. The temperature at which this takes place is the fire-point. In determining the flash-point note the behaviour of the oil. It should not foam or crack on heating. Foaming and cracking are frequently caused by the presence of water. (5) *Turbidity.*—Note whether the oil is perfectly clear or not. (6) *Foots.*—Let a litre of the oil stand in a clear glass bottle for 8 days, and then note the amount of residue formed. The highest grades of oil show no turbidity or foots by this test. The claim is made that sometimes what would be called foots by the above method is due to the freezing out of fats of rather high melting-point. When a sufficient amount of the sample is available, heat one portion to 100° C. and set it aside for the determination of foots, together with a sample just as it is received. (7) *Break.*—Heat 50 c.c. of the oil in a beaker to 300° C. Note whether the oil remains unchanged or "breaks," that is, shows clots of a jelly-like consistency. Note also the odour of the oil after cooling, and by rubbing it on the hands a small amount of fish oil may be detected in this way. (8) *Moisture.*—Heat about 5 grammes of oil in an oven at 105° for 45 minutes; the loss in weight is considered as moisture. This determination is, of course, not exact, as there is some oxidation. When more accurate determination is desired perform the whole operation in an atmosphere of hydrogen. (9) *Ash.*—Burn about 20 grammes of oil in a porcelain dish and conduct the flashing at as low a temperature as possible. The best oil should contain only a trace of ash. An amount as large as 0·2 per cent. would indicate an adulterated or boiled oil. Examine the ash for lead, manganese, cobalt, and calcium. (10) *Drying on Glass.*—Coat glass plates 3 by 4 inches with the oils to be examined, expose to air and light, and note when the film ceases to be tacky. A good oil should dry to an elastic coherent film in three days. Varying conditions of light, temperature, and moisture have such an influence on drying tests that for comparison of one linseed oil with others all samples must be run at the same time. (11) *Drying on Lead Monoxide.*—Livache's test calls for precipitated lead, but litharge gives equally good results. Spread about 5 grammes of litharge over the flat bottom of an aluminium dish 2·5 inches in diameter and five-eighths of an inch high, weigh the dish and the litharge; distribute as evenly as possible over the litharge 0·5 to 0·7 gramme of the oil, weigh exactly, expose to the air and light for 48 hours, weigh, and calculate the gain in weight to percentage based on the original weight of the oil taken. (12) *Acid Number.*—Weigh 10 grammes of oil in a 200 c.c. Erlenmeyer flask, add 50 c.c. of neutral alcohol, connect with a reflux air condenser, and heat on a steam-bath for half an hour. Remove from the bath, cool, add phenolphthalein, and titrate the free acid with fifth-normal sodium hydroxide. Calculate as the acid number (milligrammes of potassium hydroxide to 1 gramme of oil). The acid number varies with the age of the oil, and should be less than 8, though when the oil is refined with sulphuric acid it may show a higher acid number. Test for presence or absence of sulphuric acid. (13) *Saponification Number.*—Weigh about 2 grammes of oil in a 200 c.c. Erlenmeyer flask, add 30 c.c. of a half-normal alcoholic solution of potassium hydroxide, connect with a reflux condenser, heat on a steam-bath for an hour, then titrate with half-normal hydrochloric acid, using phenolphthalein as indicator. Always run two blanks with the alcoholic potash. From the difference between the number of cubic centimetres of acid required by the blanks and the determinations, calculate the saponification number (milligrammes of potassium hydroxide to 1 gramme of oil). The saponification number should be about 190. (14) *Unsaponifiable Matter.*—As the saponification varies somewhat in pure oil, it is sometimes advisable to make a direct determination of unsaponifiable matter. Saponify from 5 to 10 grammes of oil with alcoholic potassium hydroxide (200 c.c. of a half-normal solution) for an hour on a steam-bath, using a reflux condenser. Then remove the condenser and evaporate the alcohol as completely as possible; dissolve the soap in 75 c.c. of water, transfer to a separatory funnel, cool, shake out with two portions of 50 c.c. each of gasoline 88° B., wash the gasoline twice with water, evaporate the gasoline, and weigh the unsaponifiable matter. The unsaponifiable matter in raw linseed oil should be below 1·5 per cent.; in boiled oil it is somewhat higher, but should be below 2·5 per cent. (15) *Iodine Number.*—Weigh from 0·2 to 0·25 gramme of oil into a 350 c.c. bottle having a well-ground stopper, dissolve the oil in 10 c.c. of chloroform and add 30 c.c. of Hanus' solution; let it stand with occasional shaking for 1 hour, add 20 c.c. of a 10 per cent. solution of potassium iodide and 150 c.c. of water, and titrate with standard sodium thiosulphate, using starch as indicator. Blank must be run each time. From the difference between the amounts of sodium thiosulphate required by the blank and the determination, calculate the iodine number (centigrammes of iodine to 1 gramme of oil). The iodine number of raw linseed oil varies from 175 to 193, though Gill states that a pure raw oil may give a value as low as 160. Boiled oil may be very much lower. Make the Hanus' solution by dissolving 13·2 grammes of iodine in 1000 c.c. of glacial acetic acid which will not reduce chromic acid, afterwards adding 3 c.c. of bromine. (16) *Rosin Oil.*—(Liebermann-Storch Test.)—To 20 grammes of oil add 50 c.c. of alcohol, heat on a steam-bath for 15 minutes, cool, decant the alcohol, evaporate to dryness, add 5 c.c. of acetic anhydride, warm, cool, draw off the acetic anhydride, and add a drop of sulphuric acid, 1·53 specific gravity. Rosin oil gives a fugitive violet colour.

The Quantitative Composition of Linseed Oil.—The C, H, and O content of linseed oil as estimated quantitatively by combustion is not a very important factor, as it does not differ greatly from other vegetable oils. Old and partially oxidised oils contain more O and therefore less C and H than unoxidised oil. The percentage composition of linseed oil varies (1) with the method adopted in obtaining the oil from the seed; (2) extraction; (3) hot pressing; (4) cold pressing. The source of the seed also intervenes. This table shows a difference of 2 to 3 per cent. in the C and O content of linseed oil:—

TABLE SHOWING THE ULTIMATE ORGANIC ANALYSIS OF LINSEED OIL.

Analyst.	Carbon.	Hydrogen.	Oxygen.	Remarks.
Saussure . .	76·0	11·4	12·6	—
Sacc . .	78·1	10·9	11·0	Cold pressed.
Lefort . .	75·2	10·9	13·9	Hot "
Cloez . .	77·6	11·3	11·1	—
Mulder . .	76·8	11·2	12·0	Seed 1½ years old. Hot pressed.
Williams. .	75·2	10·7	14·1	Raw oil.
Bearn . .	76·2	10·6	13·2	Extracted by petroleum ether from Baltic seed.

The Average Glycerine Content of Linseed Oil. Fahrion's Glycerine Test.—The average glycerine content of linseed oil is taken as 10·4 per cent. This content with the average 95·5 of fatty acids (Hehner's No.) is in excess of 100, the glycerine and fatty acids in forming esters lose water. In calculating the analytical results a difficulty occurs as the fatty acids found are calculated as anhydrides. The mean molecular weight being of a complex nature is not accurately known.

The Respective Percentages of Liquid Unsaturated and Solid Saturated Fatty Acids in Linseed Oil.—(*a*) Solid Fatty Acids.—To solve this last problem Mulder made a series of experiments. He first extracted the lead salts by ether, decomposed the insoluble lead salts and crystallised the solid fatty acids once from alcohol. He thus found 6·3 per cent. of solid fatty acids in linseed oil. He thought this result too low, so he placed an alcoholic solution of the mixed fatty acids repeatedly and for a week in a freezing mixture until no further separation occurred. The mixed solid fatty acids so separated were crystallised once from absolute alcohol. He thus found 9·4 per cent. of solid fatty acids, but they were not pure white. Mulder designed a third method based on the insolubility in dilute alcohol of the magnesium salts of the solid fatty acids, whilst the salts of the liquid fatty acids dissolve therein. He therefore dissolved the mixed fatty acids in dilute alcohol, added ammonia to the solution, and precipitated with an alcoholic solution of magnesium acetate. After standing two days they were decomposed by H_2SO_4. He thus found 10·3 per cent. and not yellow coloured. This result was not, however, unquestionable. Fahrion repeated Mulder's experiment with 70 per cent. alcohol, and obtained quite a similar result. But this acid melted at 32° C. (Mulder gave no melting-point, but gave an iodine No. of 114·1). Separation of the saturated from the unsaturated acids in the above manner is impracticable. Mulder, however, saw in his 10·4 result confirmation of a previous result of 9·4 er cent. and asserted that linseed oil contained about 10 per c of saturated glycerides. Later on, by fractionally crystallising th lid fatty acid from alcohol, he obtained equal weights of palm. and myristic acids, so he reasoned further that linseed oil co ained 5 per cent. of tripalmitin and 5 per cent. of trimyristin. Now it chiefly contains arachidic and stearic acids; the amount of the first is very small and that of stearic acid less than 1 per cent. It is from Mulder's assumption that the solid fatty acids of linseed oil are described as consisting of ½ of palmitin and ½ of myristin. Fahrion estimated the saturated fatty acids of linseed oil by Warrentrapp's method, controlled by other methods: (1) Precipitated the neutral alcoholic ether soap solution by alcoholic lead acetate, treating the lead salt by nitric acid (Bromeis and Sacc) and extracting the resulting product with petroleum ether. (2) Oxidation of the alkaline soap solution by potassium permanganate and extraction of the oxy-acids by petroleum ether, separation of the solid fatty acids by Farnsteiner's method.

TABLE SHOWING PERCENTAGE CONTENT OF SOLID FATTY ACIDS IN VARIOUS SAMPLES OF LINSEED OIL, THEIR MELTING-POINTS IN DEGREES CENTIGRADE, AND THEIR IODINE NUMBER.

Content in Solid Fatty Acids of Linseed, per Cent.	Melting point °C.	Iodine No.
8·1	53-54	10·6
8·2	53-54	11·2
8·0	53-54	14·3
7·9	52-53	31·6
8·4	—	21·3
9 5	—	14·8
10·2	52-53	22·5
8·6	52	14·1
9·7	52	1·4
9·9	53-54	13·9

Fahrion concludes from the results given in the table that linseed oil contains, in round numbers, 8 per cent. of saturated acids.

Lewkowitsch obtained similar results by Warrentrapp's method. He first obtained 8·9 per cent. of solid fatty acids, with the iodine number of 22·3, and on again subjecting the acids to the same process, 7·5 per cent., with the iodine number of 19·2. Later, Fahrion used another method, resembling Sacc's. Instead of the soda soaps, the linseed oil fatty acids were themselves oxidised. The oxidation was affected by aid of cotton-wool, and, finally, the oxyacids were not converted into salts, but treated with petroleum ether. During the first oxidation a residue of 36·6 per cent. of fatty acids was extracted by Warrentrapp's method. Then the unsaponifiable was separated. There resulted 8·5 per cent. of fatty acids with the iodine number 6·8 and m.p. 53.

(*b*) *The Percentage of Fluid Fatty Acids, Oleic Acid.*—The fluid fatty acids were oxidised after Hazura. The unchanged portion was separated by petroleum ether, and again extracted by Warrentrapp's method. Hereby was recovered that portion of the solid fatty acids which, in the first extraction, passed into the ether solution. It amounted to 0·8 per cent. of the linseed oil, with iodine number 11·7, m.p. 49·5. Under the assumption that both iodine numbers, so found, are exclusively due to oleic acid, that reduces the percentages 8·5 and 0·8 to 7·9 and 0·7, and the mixed solid fatty acid content of linseed oil would then be 8·6 per cent. This percentage for the linseed oil in question approaches those in the above table very closely. Whether the fatty acid content of different linseed oils shows greater deviation, further research must elucidate. The content of linseed oil solid fatty acids may be calculated from the [illegible] iodine number (*a*) and the inner iodine number (*b*), not ex- 10·4 per [illegible]ver, as the inner iodine number comes out too low. As (Hehne[illegible] glycerine absorbs no iodine, it follows that $\frac{100\,a}{b}$ gives the percentage content of solid fatty acids in linseed oil, including the unsaponifiable, which also absorbs iodine. In a research by Fahrion he found the iodine number of the linseed oil 180·9, the Hehner number 95·7. Calculation gives the high iodine number of 205·2, leaves 87·7 of fluid fatty acids, therefore 95·7 − 87·7 = 8 per cent. solid fatty acids. Walker and Warburton's figures give 7·3. Those of Tortelli and Ruggeri are therefore too low.

Mulder believed he had detected oleic acid quantitatively; the research in question gave repeatedly 10 per cent. of the linseed oil, besides the oleic acid. The last research only gave 8 per cent. Mulder did not make any separation, he assumed linseed oil to contain triolein, therefore, 9·5 per cent. oleic acid. Hazura only found half as much. He obtained by the alkaline oxidation of 100 grammes of linoleic acid, 1·2 dioxystearic acid; 6·5 sativic acid; 20·3 of linusic and isolinusic acids. From these figures he counted backwards; thus the fluid linoleic acid consisted of 5 per cent. of oleic acid, 15 per cent. of linoleic acid, and 80 per cent. of linolenic and isolinolenic acids. This conclusion is incorrect. Fahrion claims that much of the linoleic acid is not quantitatively oxidised. Part of it is not attacked, and much of this unaltered portion consists mainly of oleic acid. A very convenient material for extracting unchanged acid was found by Fahrion in petroleum ether, in which dioxystearic, sativic, linusic, isolinusic, and azilaic acids are completely insoluble. In two oxidation experiments, exactly according to Hazura's method, 15·4 and 16·4 per cent. of the linoleic acid remained unchanged. The iodine number showed 85·3 and 78·2. But the manganese precipitate was not washed out, so that the above percentages are still small. That the residue from the oxidation consists chiefly of oleic acid follows at once from the iodine number, oleic acid = 90; linoleic acid = 181·6; linolenic acid 273·6. But the result of a second oxidation left dioxystearic acid, and gave 38 per cent. yield. Pure oleic acid oxidised in the same way left 65 per cent. From the above figures linoleic acid contains, not 5 per cent., but 20 per cent. of oleic acid.

This figure seems to agree with the above oxidation experiments. On extraction by Warrentrapp's method 8·5 per cent. of solid fatty acids was obtained, and 24·1 per cent. liquid fatty acids with the iodine number 105·3. Therefore, there were only traces of linolenic acid, of which 0·8 per cent. was solid fatty acids. The iodine number calculated to 19 per cent. of oleic acid yielded 9·7 per cent. of dioxystearic acid, which calculation gives 15 per cent. of oleic acid, where pure oleic acid gives 60 per cent. Seventeen per cent. of oleic acid may be taken, but the average is between 15 and 19; that leaves, in round numbers, about 70 per cent. for the linoleic and linolenic acids of linseed oil. If 180 be taken as the mean iodine number of linseed oil, then the 70 per cent. may be calculated as 27 per cent. linoleic and 43 per cent. linolenic acid. Numerous researches prove that the iodine number of oxidised linseed oil is lowered as far as 172·3. During oxidation 36·6 per cent. of linseed oil, with the iodine number 86·7, remains. The Hehner number of the original oil is 95·6. The linoleic and linolenic acids are lowered to about 59 per cent. The iodine number of the altered mixed fatty acids may be calculated as 238·3; and this number, on further calculation, gives for the 59 per cent. 36·4 linolenic acid, and 22·6 linoleic acid. In the first extraction (after Warrentrapp) there was a loss of 4·0 per cent., of which the smaller portion may be taken as linolenic acid, so that it gave 38 per cent. linolenic acid and 30 per cent. linoleic acid.

THE PROXIMATE CHEMICAL COMPOSITION OF LINSEED OIL. (FAHRION.)

	Per Cent.
Unsaponifiable	0·5 to 1·5
Saturated fatty acids	8·0 ,, 9·0
Oleic acid	15·0 ,, 20·0
Linoleic acid	25·0 ,, 35·0
Linolenic acid	35·0 ,, 45·0
Glycerine	4·0 ,, 5·0

According to Hazura the above linoleic acid content given by Fahrion is too small. He found 80 per cent. of linoleic acid which gave 70 per cent. on the linseed oil. On bromination of the linoleic acid he obtained a crystalline hexabromlinolenic acid, with a maximum yield of 40 per cent., whereas he gives 15 per cent. of linolenic acid in linoleic acid, which gives 13 per cent. on the linseed oil. Isolinolenic acid must therefore be present to about 57 per cent. in linseed oil itself. Hazura states that it gives an amorphous hexabromide soluble in ether. On their existence depends that of isolinusic acid which is produced from it.

A. Rollet calculated for linseed oil, on the basis of the iodine number of 190, a solid glyceride content of 15 per cent., and a linolenic acid content of 50 to 60.

All other authorities on oils stop short at 35 to 45 per cent. of linolenic acid as the highest, Fokin, by bromination of the mixed fatty acids, under various conditions, 22 to 29 per cent. of crystallised hexabromide and 22 to 25 per cent. of linolenic acid, but, as Fahrion points out, this must be a printer's or other error, as hexabromlinolenic acid, $C_{18}H_{20}Br_6O_2$, contains 63·3 per cent. bromine, so that the above figures only correspond to an 8 to 10 linolenic acid content of linseed oil of solid fatty acids. Fokin gives only 5 per cent., and explains it on the supposition that linoleic acid is the chief constituent of linseed oil. He sees nothing more in the crystallised tetrabromide of m.p. 114° C. than that the linoleic acid of linseed oil differs from that of poppy-seed oil, whilst Hazura regards them as identical, since both on oxidation leave sativic acid. Lewkowitsch obtained 42 per cent. of a crystallised hexabromide as a maximum from the mixed fatty acids of linseed oil, and calculated therefrom that there was 15 per cent. of linolenic acid in linseed oil. That this content agrees well with the iodine number is not to be disputed but it seems low. Like Fokin, Lewkowitsch regards linoleic acid as the chief constituent of linseed oil. F. Bedford prepared the crystallised hexabromide from the mixed fatty acids of linseed oil with a yield of 41·6 per cent. or 15·27 per cent., calculated as a linoleic acid, or 14½ per cent. on linseed oil. He used the reduction method, with nickel as catalyst, as an analytical process. By its aid he estimated the hydrogen number of substances, calculating the hydrogen required for complete reduction, to per cent. For ethylic linolenate obtained by bromination, from the hexabromlinolenic acid ester he found the data 1·9482 and 2·0480, theory 1·9737. The ethyl-ester from Farnsteiner's separated linoleic acid, gave hydrogen numbers 1·4544; 1·4578; 1·4441. Therefore the theoretical hydrogen number of ethyl linoleate comes out 1·3072. So calculated from the above figures the esters investigated had an average content of ethyl-linolenate of 21·7, which gave for linseed oil a linolenic acid content of 15·0. Likewise, the iodine number of the fluid fatty acids are given by Erdmann and Bedford in a continuation of Rollet's work as 203·8, which corresponds with a content of 24·4 per cent. instead of 21·7. Then the yield of hexabromlinolenic acid is so increased that they correspond to a linolenic acid content of the mixed fatty acids of 16·66 per cent. Calculated to linseed oil this becomes 15·8 per cent. However, Erdmann and Bedford give a content of 20 to 25 per cent. acids, $C_{18}H_{30}O_2$, chiefly, but not exclusively consisting of a linolenic acid, yet, during debromination, hexabromlinolenic acid splits up into two stereoisomeric linolenic acids. Fahrion points out that Bedford found as the iodine number of free linolenic acid instead of 273·8, 248·1, and that the iodine number 203·8 of the mixed fatty acids is also too low. Lewkowitsch found, for the Warrentrapp prepared acids, which still contained oleic acid, the iodine number of 209·8. The hydrogen number, however, correctly estimated, does not give correct results, as by Farnsteiner's method the solid fatty acids are not quantitatively removed from the oleic acid. This Fahrion proved experimentally when he tested Bedford and Farnsteiner's linoleic acid by vacuum distillation; 4·5 grammes of his acid were treated with 4·5 grammes of $KMnO_4$ after Hazura's instructions. During the acidulation of the filtrate, the precipitate which settled out was dried first with petroleum ether and then extracted with much cold ether. The evaporation residue of the petroleum ether extract of the unoxidised portion gave, on crystallisation from alcohol, a small amount of solid fat of m.p. 54. The evaporation residue of the ether extract likewise gave a product that could not be crystallised from alcohol, the oxidation product of oleic acid, dioxystearic acid, m.p. 129. Finally, Bedford obtained, during the reduction, a fluid product; again, the fatty acids of linseed oil on heating, even without oxidation, decreases in acidity and their iodine number lowers. Also during the heating of linseed oil its hexabromide number is lowered. Is it the α or the β-linolenic acid that remains on heating? In either case it would not be an isomer but a variety of the same product. The variety must be regarded in the nature of things as an altered part of the double bond.

Effect of Storage of Linseed Oil on (1) *its Acid Value*, (2) *its Density*, (3) *its Refraction.*—The storing of linseed oil does not result in the mere splitting off of glycerine alone. The gravity of a 13-year-old sample was 0·941 (Lewkowitsch), which is above normal by 0·009. A 5-year-old sample had a butyro-refractometer degree of 85·1. Fresh raw oil gave 80 to 81·5° Weger. In a fresh oil with the high iodine number of 191·3 and oxygen number of 19·8 the original acid number rose from 1·8 to 2·7, an increase due to the lowering of the iodine number. Spollema kept two samples of the same linseed oil in the dark, one refined by H_2SO_4, the other not, in well-corked flasks. The iodine in No. 1 did not appreciably lower, whilst in No. 2 it lowered about 10.

The painter protects the linseed oil vehicle of his paint from the air by a surface layer of water inside the keg.

So little does the painter desire that his linseed oil should become oxidised during storage, that he shields it, as regards stiff paints, by protecting them with a layer of water. Mulder ascribed the change which linseed oil undergoes during storage to a certain amount of the glycerine being decomposed and the remainder locked-up. Stored linseed oil becomes partly acid and rancid, but it does not follow, from its oleic acid content, that such oil is by any means rancid. Mulder ascribed this rancidity to an activity of motion in effective matter, e.g. quite a small amount of albumin present in most oils and fats. The precise chemical process consists in the splitting-off of glycerine with the consequent oxidation of the free fatty acid, especially the oleic acid to butyric acid. This opinion of rancidity is similar to that held at the present time. Geitel defined rancidity of oils as induced by an oxidation process begun by light, with splitting-up of the water from a minimum but sufficient quantity. Pure oil or fat shielded completely from air and light does not turn rancid. Fats from the tombs of Abydos were examined by Friedel and the glycerides therein found to be undecomposed. But the action of antiseptics may have intervened to preserve the glycerides in their pristine state as well as mere protection from light. When an oil or fat is mixed with the marc of the fruit, i.e. with oil cakes or albuminoids, hydrolysis of the oil or fat sets in and the amount of free fatty acids increases. The cause is the combined action of water and enzymes. The question why linseed oil, notwithstanding its richness in unsaturated fatty acids, rancidifies with difficulty, was answered by I. Klemont to the effect that here the oxidation produced is so strong that atmospheric gases cannot act. Freshly spread out linseed oil often smells of oenauthylic-aldehyde and octyl-alcohol.

Tortelli and Pergami's Theory of the Changes Supervening in Old-tanked Oil.—Tortelli and Pergami assert that, during the storage of linseed oil, a sort of molecular absorption occurs, the fluid fatty acids playing the chief rôle. Thus, in old linseed oil, a portion of the glycerides have a different constitution than when fresh. When the free fatty acids are completely removed from old oil they dissolve more readily in alcohol than the fatty acids from fresh oil.

The Deposition of Foots, Mucilage, etc., from Old-tanked Oil.—There generally separates from unrefined raw oil, during storage, a deposit of variable composition. Suspended matter may be deposited completely, dissolved mucilage is never completely deposited by storing or tanking. A pale old-tanked English oil still showed mucilage on heating after five years (Weger). Now the presence of this mucilage, which contains the above organised bodies, enzymes, which can induce the splitting-up of the oil is, for obvious reasons, as mentioned elsewhere, far from desirable.

Effect of Storage of Linseed Oil (Old-tanked Oil) on its Acid Number and its Iodine Number.—On this point a whole series of authorities declare that the acid number of linseed oil protected from air increases without inducing any chemical change. Hubl found in a 15-years-old sample of linseed oil the normal iodine number, whilst an oil, which under the action of the oxygen of the air had become viscous and rancid, gave low results. Thomson and Ballantyne left samples of linseed oil with the iodine number 173·5, (*a*) for six months in sunlight but in a closed flask, (*b*) with access of air; the first (*a*) fell to 172·9, that of the second (*b*) to 166·2. Lettenmayer and Niederlander still found in a Dutch linseed oil 19 years old, kept in a completely filled, well-corked flask, the iodine number of 180·2, whilst in a 30-years-old Dutch linseed oil, of which only a small quantity was contained in a large flask, the iodine number was 156·2 and the acid number 1·50. Again, a sample of linseed oil shielded from air and light for three years gave iodine number 174·0 and acid number 1·3; a Baltic oil 13 years shielded from air and light the iodine number 175·8 and the acid number 7·2. Sherman and Falk found that linseed oil kept in quite full flasks and protected from air and light for months did not change.

BOILED OIL.

Finkener's Method of Differentiating Between (a) *Raw and* (b) *Boiled Oil.*—Finkener gives a qualitative method for differentiating between (*a*) raw linseed oil and (*b*) boiled linseed oil, in which it is shaken with an aqueous solution of lead acetate, glycerine, and ammonia. With raw oil the aqueous layer is clear, with boiled oil it is turbid. The method depends on the presence, in the boiled oil, of free fatty acids, to a greater or less extent, and is rarely used. According to Evers it is most applicable to lead oxide boiled oils.

Mopurgo's Method.—Another method by Mopurgo is given. Five grammes of the oil to be tested are saponified by alcoholic soda, the alcohol evaporated, the soap dissolved in water, and, in the soap solution, common salt is dissolved until no more soap separates. The filtrate is decomposed by acetic acid. With pure raw linseed oil no precipitate occurs, but it does with boiled oil. The method does not go further than the qualitative detection of the unsalted out oxy-acids. It cannot be used with cold prepared "boiled" oils, and is only applicable to strongly blown oils, or oils oxidised during boiling.

The Water Reaction.—The water reaction may be used for the qualitative testing of boiled oil for purity. One c.c. is saponified with alcoholic potash and the soap solution diluted with much water on flasks. The iodine in No. 1 did not appreciably lower, whilst in No. 2 it lowered about 10.

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The Iodine Absorption Number of Boiled Oils.—The iodine number of boiled oils, made from soluble driers, remains as high as in raw linseed oil, e.g. McIlhiny found 180·4 to 183·3. However, the iodine number (1) ordinary boiling, (2) by blowing, and (3) by the addition of mineral oil, is lowered. The lowest range for pure boiled oil according to Filsinger is 160, Hefelmann and Mann 163, Ulzer 145, Charitschkoff 130. The iodine number of boiled oil does not play the great rôle that it does during raw oil examination. In estimating the iodine number of boiled oils the metals should be previously removed and higher numbers are then found.

The Hexabromide Number of Boiled Oils.— The data as to the hexabromide number of boiled oils ought to tell us whether the boiled oil was boiled at a high temperature or prepared in the cold. Investigations on this point have not been made hitherto. The figures in the accompanying table were determined by Lewkowitsch :—

TABLE SHOWING FIGURES FOR RAW LINSEED OIL, PALE AND DOUBLE BOILED OILS, AND OZONISED OILS.

	Density 15° C.	Iodine No.	Hexabromide No.
Raw linseed oil . .	0·9308	186·4	24·17
Pale boiled oil . .	0·9429	171·0	20·97
Double ,, . .	0·9449	170·0	13·03
Ozonised ,, (I.) . .	0·9310	180·1	36·30
,, ,, (II.) . .	0·9388	171·2	25·73
,, ,, (III.) . .	0·9483	169·7	30·19

The Oxygen Absorption Number of Boiled Linseed Oil.—The data as to oxygen absorption in boiled oil examination is scanty. Cold prepared or only slightly heated boiled oils generally give as high absorptions as the raw oil. Strongly boiled and strongly blown oils show lower numbers, but they cannot be differentiated by the oxygen numbers. All that can be said is that the first takes longer to dry, and that the maximum increase eventually is as high as in the case of the latter.

The Estimation of the Oxyacids in Boiled Oil.—The estimation of the oxyacids is undoubtedly established on a sound basis although it has as yet come little into use. As already pointed out their amount increases during boiling without air blowing, and to a far greater extent by blowing, and by storing with access of air. Small amounts of oxyacids may be ascribed to rosin or rosinate driers.

The Unsaponifiable Content of Boiled Oil.—It was formerly believed that, during oil boiling, the amount unsaponifiable increased. R. Williams found in raw linseed oil 0·8 to 1·3, in boiled oils 1·3 to 2·3 unsaponifiable. It was soon found, however, that during oil boiling and blowing no considerable increase of unsaponifiable content occurred. Ulzer only found in oxide-boiled oil 0·5 to 0·92 per cent. unsaponifiable. Rosin contains much unsaponifiable, so that in rosinate-boiled oils a slight increase of the original unsaponifiable content occurs. O. Bach found in oxide-boiled oils 0·43 to 0·74. In rosinate-boiled oils 0·95 to 0·71 per cent. unsaponifiable.

It is agreed to take 2 per cent., as the highest limit of the unsaponifiable content. With higher contents the iodine number of the unsaponifiable is determined. It sinks with pure boiled oil below 70 to 80 per cent., whereas rosin oil, and particularly mineral oil, tends to further decrease. Generally less than 2 per cent. is found, and then hydrocarbides are present. G. Knappe found in a boiled oil 2 to 3 per cent. which was detected by its smell during the water reaction making itself felt. Moreover, tested in the Abel Pensky apparatus at 80 to 90° C. (176 to 194° F.) an undoubted flash occurred. H. Wolff found the saponification number 188·5, the butyro-refraction degree 87, and the density 0·9309. Drying was normal, the unsaponifiable was 1·2. However, the boiled oil contained 4 per cent. of light benzine driven off by steam distillation. Finally, "boiled oils" prepared by the aid of liquid driers contain a certain percentage of turps or white spirit, which is best removed by steam distillation.

The Twitchell-Wolff Method.—That this method is peculiarly adapted for the estimation of rosin in boiled oil has been proved without doubt. Now as fused rosinates are the driers most generally used, the question must be answered: How much rosin, free and combined, must a genuine boiled oil contain? The question has been answered by C. Niegemann who asserts that 5 per cent. rosinate suffices under all conditions, and that any higher content must be regarded as adulteration. As much as 7 per cent. rosin acids, when ground with white lead, causes "livering". According to H. Wolff, 3 to 4 per cent. suffices and 6 per cent. is too much. But rosin-free or combined, i.e. in any shape or form, in the present author's opinion, is an illegal addition to boiled oil.

Viscosity.—In forming or giving an opinion as to a boiled oil it is well to determine its viscosity.

Separation for Subsequent Estimation of Rosin and Free Fatty Acids in Boiled Oil.—About 10 grammes of oil are weighed and dissolved in 100 c.c. petroleum ether, and the solution shaken twice with dilute HCl; water is added to wash free from acid, then 50 c.c. neutral alcohol, also phenolphthalein. The whole is titrated with N/10 alkali to neutral; water added to dissolve resulting soap; shaken and set aside. The soap solution is run into another separator, and treated with 50 c.c. petroleum ether, shaken, soap solution run off, and petroleum solution added to first separator. Soap solution is returned to second separator and purified by treating with 20 c.c. 50 per cent. alcohol. The residual lye solution evaporated to dryness is next dissolved in water, agitated in a separating funnel with petroleum ether and dilute HCl; next, washed free of acid. The fatty and rosin acids are obtained after evaporation of petroleum ether. Such residual acids are then available for determination by the usual known methods. The first petroleum ether solution contains the neutral saponifiable linseed oil, likewise the unsaponifiable mineral and rosin oils—all being recoverable for examination by evaporation of the ether.

TABLE SHOWING CHANGE OF CHEMICAL CONSTANTS THROUGH BOILING OF LINSEED OIL.

No.	Acid Value.	Saponification Value.	Iodine Value.	Iodine Value of Fatty Acids.	Acetyl Value.
0	4·8	188·9 188·6	159·3 158·6	158·0	153·5
1	5·2	189·9 188·3	101·4 100·1	107·3	191·3
2	7·8	189·1	95·6	100·1	192·4
3	9·5	186·6	83·6	88·1	188·2
4	9·1	187·2	79·1	85·6	—
5	11·7	187·2	76·2	81·9	193·4 192·6
6	18·8	192·3	71·1	—	—

Nos 0 to 6 show the changes from the thin raw oil to the consistency of caoutchouc.

Boiled Oil Adulterated with Rosin Oil. Weger and Bach's Experiments.—Rosin oil has an irregular lower iodine number than rosin. Everything connected with rosin oil varies with the sample—crude rosin oil and refined rosin oil are two different things. According to Weger rosin oil gives a loss in two months of 15 to 26 per cent. in weight. However, taking boiled rosin oil in which 6 per cent. lead-manganese rosinate was dissolved at 120° C., oxygen absorption numbers of 19·8 to 25·7 inner-half were found in 5½ to 8½ days. Drying proceeded quickly, in 1½ to 2½ days. It is thus differentiated from boiled linseed oil by the fact that the maximum in weight takes longer. Weger worked with almost acid-free rosin oil. Acid number 0·9, density 0·98. No iodine number is given. For pure rosin oil he found negative numbers, due possibly to refining rectifications and removal of impurities by washing, also to considerable volatilisation of secondary products. An experiment of O. Bach contradicts this. He heated a gun barrel, which contained 1 gramme of rosin oil in a sealed tube with excess of oxygen, for 10 hours, at 110° C.; 181 c.c. of oxygen were absorbed, which means an oxygen number of 25·9. The use of rosin oil has been the subject of many patents, mostly worthless.

Adulteration of Boiled Linseed Oil with Rosin.—With the small amount of rosin in rosinate-driers used in oil-boiling, it is interesting to learn how it affects the drying of the oil. Rosin is not inert, far from it. It finds expression in the higher iodine number as the linseed oil absorbs oxygen from the air. Weger proved this directly, and indirectly. He mixed boiled oil in large quantity with American rosin and tested the mixtures on glass plates. The oxygen number of the contained rosin did not sink, at the most, below the oxygen number for rosin of 8·2 for the period of 20 hours heating at 150° C.; rosin showed an oxygen number of 11·7. Finally, an alcoholic rosin solution in a crystallising dish was evaporated, the residue heated for an hour at 100° C., and (*a*) solution, (*b*) evaporation, and (*c*) heating continued five times. The rosin increased 7·6 in weight. By further heating it lost in weight, owing to the volatilisation of secondary oxidation products. Fahrion left 1 gramme of ground rosin on a watch glass with frequent stirring without loss, at summer temperature, for two months, exposed to the air. The whole thickness increased 4·2 per cent. But the autoxydation product of rosin has not got the good properties of linoxin. Moreover, much rosin in boiled oils renders the dried oil films tacky; besides it has frequently been recorded that mixing such boiled oils on the basis of these and similar figures with white lead, or with paints containing white lead, causes energetic thickening (livering).

Peculiarities in the Drying of Fish Oil.—The drying capacity of fish oil was tested by Meister on glass plates. Drying starts much more rapidly than with linseed oil, and is generally complete in 24 hours. The oxygen figures give no curve; when added to linseed oil the drying of the latter was not accelerated. After two days the increase in weight was accompanied by loss in weight and the nett weight remained constant, then regular decrease followed. The maximum increase occurs, as with linseed oil, when the oil has just dried. The oil skins of walrus, whale, and cod oils are peculiar. Only in the case of certain fish oils is the oil skin uniformly solid; in all cases such solids are completely soluble in chloroform and ether and only withstand atmospheric influences poorly. Driers accelerate drying action, but the period of drying or hardening is about twice the length of time requisite for linseed oil. However, the oxygen absorption numbers are higher than for pure fish oil. On the basis of his experiments, Meister limits the percentage of fish oil in a boiled oil to 25 to 40 per cent. of the boiled oil, and recommends the mixture, to be made at 140° to 150° C. with 5 per cent. of fused lead-manganese rosinate, or 2·5 per cent. of precipitated rosinate of manganese, being used as drier. The boiled oil so remains pale and bright, whilst pure fish oil heated alone with driers darkens greatly, and deposits foots copiously.

As examples, Meister gives the oxygen absorption numbers for a sardine fish oil (iodine number 183·4), for the boiled oil made from it, and for a boiled oil with 75 per cent. linseed oil and 25 per cent. fish oil. Parallel with these are shown the figures for a raw linseed oil and the pure boiled oil made from it.

Boiled Oil Adulterated with Mineral Oil.—In contrast to rosin and rosin oil, mineral oils with their low iodine absorptions absorb no oxygen from the air. Lippert found that several samples contained no ingredients volatile in the air; no oxygen absorption number was obtained. Speaking generally an addition of mineral oil to boiled oil lowers the oxygen number; the time of drying may remain the same, the time of "setting" may even be accelerated. Lippert describes a motion of the inner half of the film; a separation of the mixture occurs and the mineral oil rises to the surface. Five per cent. of mineral oil can readily be detected by the finger, as the boiled oil skin remains behind whilst a pure linseed oil adheres. Lippert made a series of experiments on petroliferous boiled oils of which the following are examples:—

ACTION OF MINERAL OIL ON BOILED OILS. RETARDATION OF DRYING.

	Time of Drying, Hours.	Oxygen Absorption No.
Manganese oxide boiled oil	24	14·4
„ „ „ with 5 per cent mineral oil	24	13·4
„ „ „ „ 10 „ „	24	13·3
„ „ „ „ 25 „ „	24	10·0
„ „ „ „ 50 „ „	72	4·7

A more extended table is given by Andés, but as it teaches no useful lesson it is not reproduced here.[1]

In a later paper Lippert shows that the depreciation of boiled oil adulterated with mineral oil is not manifest. Small quantities of the latter form on the surface of dried boiled oil a fine layer of the boiled oil skin which still combines with it and partially envelops it. The mineral oil is not tacky. Such a film is as good and lustrous as a pure boiled oil. But Lippert is absolutely wrong in this respect—that the direct heat of the sun will sweat the mineral oil out in greasy streams, the flow of which down a vertical coat of paint is most unsightly, and that, too, if the film is perfectly hard and consistent in cold weather. Mineral oils have their use, but that is neither in paint nor varnish films. On the other hand, the mineral oil does not dry, the coat is not tacky but very soft. It is neither boiled oil nor paint but a grease. When, however, a good boiled oil is required for floors which is neither tacky nor cracks, mineral oil added to the boiled oil, Lippert claims, prevents such defects. If the layer of mineral oil on the boiled oil is but thin, it is eventually dissolved by the boiled oil and partially enveloped therein, and partly used up to form the new surface. The boiled oil therefore does not dry properly, it remains soft and soon becomes unsightly, especially when exposed to the heat of direct sunlight, when the coat of paint is covered by tiny eruptions like a miniature lake of asphaltum. Lippert is in this case of mineral oil in boiled oil quite unintelligible, and its addition is so obviously senseless that even to chronicle the merits and defects of the mixture is preposterous.

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[1] The author has yet to meet the painter that would use a boiled oil with even 5 per cent. mineral oil; it would be continually oozing and sweating out of the paint.

Boiled Oil Foots.—A good boiled oil should be pale. It darkens the more the longer it is heated. The number of driers affects the colour, particularly manganese driers; soluble driers give a pale colour. During blowing, boiled oil is bleached to a certain extent; likewise, during oil-boiling, mucilage is eliminated. A good boiled oil should be clear and mucilage-free. Small quantities of foots may form, but such quickly subside. A percentage of mucilage, it is claimed, does not alter the drying capacity of the oil, but those who argue so forget it robs the oil of its driers, and not only so, mucilage may start a process of decay when exposed to sunlight of which we know nothing. Pure lead-boiled oil shows a very bulky deposit of foots. Pure manganese boiled oil does not. Again the use of lead as rosinate forms no foots, so long as the amount of the latter is not too great. According to Lippert lead-boiled oil remains clear, with complete exclusion of air. The composition of boiled oil foots has not been satisfactorily determined. Lippert believes that during the boiling with lead oxide, lead glycerinates are formed, simultaneously with foots. Yet he regards the foots as an oxidation product which remains on treatment with air. That may be so to some extent, but not necessarily. Everything points to other sources, mucilage, solid fatty acids, insoluble metallic soaps, oxidised fatty acids, either free or combined with metallic oxides.

The Polarimetric Examination of Boiled Linseed Oil.—The behaviour of boiled oil under the action of polarised light may be used specially for the determination of rosin and rosin oil therein. Filsinger advises that boiled oil can be rendered paler by dilution with 2 volumes of chloroform and 1 volume of absolute alcohol. Pure oxide and linoleate boiled oil only give a minimum deviation, rosinate boiled oils give a higher. Filsinger found boiled oil containing rosin to give a deviation of + 25° up to + 30°.

Effect of Blowing of Linseed Oil on its Hexabromide Number.—But more important than all the above is the discovery of Hehner and Mitchell that during the oxidation of linseed oil by blowing its hexabromide number decreases.

The Chemical Changes which Supervene During Storage of Linseed Oil and on Heating Without Access of Air.—What chemical change supervenes during the storage of linseed oil is an important point, complicated by the fact that the same changes in much greater masses of oil supervene when linseed oil is heated without access of air, and heating without access of air eventually ends in dry distillation. Mulder proved by his dry distillation experiment, and generations of printing-ink makers long long before him, that linseed oil when heated gradually thickens and eventually passes into a glutinous mass used as bird-lime. We shall see later on that Jonas heated this "bird-lime" with nitric acid to render it more solid and glutinous, a sort of rubber soluble in aqueous potash lye, also in much turps. Sacc heated linseed oil in a retort, and a white vapour thickened in the neck of the retort with a smell of fish. Later on brown products distil until the oil changes to a resinous rubbery mass.

CHAPTER X.

THE TECHNICAL CHEMISTRY OF LINSEED OIL. MANUFACTURE OF PRINTING INK.

Action of Heat on Linseed Oil. Partial Dry Distillation of Linseed Oil.—Mulder subjected raw linseed oil to partial dry distillation by keeping it in a retort for 36 hours at nearly boiling heat, but he did not allow any trace of carbon to separate. In the first 6 hours 5 per cent. of the oil came over with the smell of acrolein, at first in fluid drops and then of a buttery consistence. In the second 6 hours another 5 per cent. came over as a white buttery mass. From that time onwards the quantity of distillate decreased so much that when the 36 hours were up almost nothing further had distilled. The distillation residue ceded very little to ether, and left, when viewed through a thick layer, a viscous dark-coloured rubber-like mass which was straw-yellow in thin layers. Mulder termed it artificial bird-lime. He subjected several samples to elementary analysis with the following combustion results:—

TABLE SHOWING THE ELEMENTARY ANALYSIS OF ARTIFICAL BIRD-LIME.

	C.	H.	O.
Found	79·1-79·9	11·1-11·4	8·7-9·7
Calculated for linoleic anhydride, $C_{32}H_{54}O_3$ . .	79·2	11·2	9·6
,, ,, linolenic ,, $C_{36}H_{58}O_3$ . .	80·3	10·8	8·9

The rational interpretation of Mulder's fractional distillation results seems to be to render the polymerisation theory of oil boiling a still-born theory, a theory which ought to have been stifled at birth. Polymerisation, as applied to Mulder's artificial bird-lime, which is linseed oil less 10 per cent. of something else, is absurd. In a polymerised product that 10 per cent. should still remain. What was the weight left in the retort of this artificial bird-lime? The record is silent. Mulder's experimental fractional distillation wants repetition. His results served his purpose. They do not serve ours. *Inter alia*, we want to see the destructive distillation results, not only of linseed oil carried to pitch, but also of artificial bird-lime itself.

From the combustion results of bird-lime Mulder thought he had obtained the anhydride of linoleic acid, and, as the formula C_4H_7 was then given to rubber, so he looked upon the anhydride of linoleic acid as an oxidation product of rubber. In the distillate Mulder claimed to have found: (1) palmitic acid, m.p. 62° C.; (2) myristic acid, m.p. 53° C.; (3) sebacic acid, $C_{10}H_{18}O_4$, m.p. 125° C.; (4) acrylic acid, and (5) various fluid fatty acids, amongst them (6) capric and (7) caprylic acids, finally hydrocarbides, which he did not further investigate. Mulder further claims from the above distillation data that the whole of the glycerine was split off, that the acrolein was oxidised, that the palmitic and myristic acids passed over as such, that the oleic acid was oxidised to sebacic acid, acrylic acid, etc., whilst from the linoleic acid water was split off and the acid remained behind in the form of linoleic anhydride. This linoleic anhydride, dissolved in potash and precipitated with acids, gave linoleic acid, also a thin fluid oil, leaving, after this treatment, according also to Mulder, a glutinous, elastic, shrivelled mass, completely soluble in ether, leaving behind on distillation of the ether a resinous substance only slightly soluble in absolute alcohol. Mulder explained this behaviour on the assumption that the linoleic acid was "polymerised" to an acid, $C_{32}H_{56}O_2$, with double the molecular weight. There can now be no doubt that Mulder's anhydride of linoleic acid was not a simple body and probably still contained glycerine. Mulder obtained quite another result when he heated linseed oil to a high temperature in a retort. There first came over (1) a small quantity of combustible gas; then (2) 3·8 per cent. of the whole mass passed over as a pale watery white fluid with a strong odour of acrolein; (3) on standing the distillate became coloured and deposited crystals. The supposed anhydride of linoleic acid also behaved similarly on heating to a high temperature. It also left a perceptible amount of a water-white distillate which became coloured on standing. Mulder did not examine the latter further but believed it to consist of hydrocarbides. It may confirm Mulder's assertion when it is stated that Sattler, on dry distilling linseed oil, produced

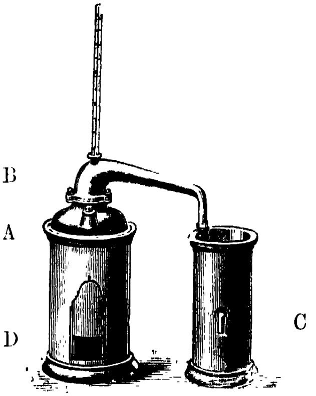


FIG. 72.—Still for the destructive distillation of linseed oil, fitted with thermometer, still head, and pipe leading to condenser.

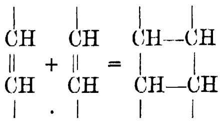
A = body of still; B = still head; C = condenser; D = furnace for heating still.

petroleum hydrocarbides, whilst Tilden obtained C_5H_8 or ± coprene. The thick oil, got by boiling linseed oil, without driers, in oil-boiling pots, with lids, and thus shielded from air, was so prepared centuries ago, chiefly for use as printing-ink vehicles. Raw linseed oil generally contains traces of water, which are evaporated at 130° C. (266° F.). This temperature, formerly known as the boiling-point of linseed oil, is still so known to some extent. But in the manufacture of thickened oils higher temperatures are necessary, and a thermometer is used to measure these instead of the burnt-feather test. The latter was dipped into the hot oil to see whether the heat singed or shrivelled it, or not. Mulder gives 310 to 320° C. (590 to 608° F.), but indicates later that the temperature for thick boiled oil is appreciably higher. Weger declares that boiling oil in this way, viz. by bubbling air through it, is not practicable at a lower temperature than 330° C. (626° F.). However, Livache gives 250 to 270° C. (482 to 518° F.) as the right heat to use for lithographic printing-ink vehicles. When the boiling is finished the vapour is set on fire and left to burn for a short time. In Great Britain this product is termed "Burnt Oil". On the Continent, thickened oils are known as "Stand Oil," "Thick Oil," "Printing Ink," "Boiled Oil," "Lithographic Boiled Oil".

ANALYSIS OF THREE THICKENED OILS FROM A PRINTING-INK FACTORY COMPRISING THREE DIFFERENT PHASES OF THE OIL-BOILING PROCESS. (FAHRION.)

Sample.	Acid Number	Iodine Number.	Oxyacids, per Cent.
A. Thin and fluid .	13·4	101·3	0·5
B. Thick and tacky .	24·9	77·3	4·1
C. „ viscous .	32·6	73·7	7·6

Glycerine was of course split off during the oil-boiling, but sample C. must still have contained the greater part of its original glycerine. Here no sure conclusion can be drawn from the acid and the saponification numbers; therefore it is not evidence that a portion of the free carboxyl groups have been changed by formation of esters. From the oxyacid content it is evident the air was not rigidly excluded. Again, the absorption of the oxyacids was in no way proportional to the decrease in the iodine number. This decrease must, therefore, have another cause than oxidation. It is ascribed to "Polymerisation," the aggregation of various molecules with one another in the place of the double bonds:—



$$\begin{array}{ccccc} | & & | & & |\quad\;\; | \\ CH & & CH & & CH-CH \\ \| & + & \| & = & |\quad\;\; | \\ CH & & CH & & CH-CH \\ | & & | & & |\quad\;\; | \end{array}$$

Confirmation of this hypothesis is supposed to be found in the fact that the above-mentioned products B. and C. from the same thickened oils were different. All were of syrupy consistency, whilst B. and C. were tacky, and left long thin strings, a property which disappears in the oxidised oil. But the latter has the property of mixing with water, to form an emulsion, which does not occur with polymerised oils. For some time the term "polymerisation" has appeared both in trade journals and in textbooks, and is very evidently grossly and systematically misused by not too well-informed writers, who hide a general lack of knowledge by language calculated to impress. Fahrion complains: "One (the man in the street) cannot understand Lewkowitsch when he writes that the chemical changes which supervene during the thick boiling of linseed oil are not completely understood, and yet classifies them under the term 'polymerised oils'".

Some years ago, Leeds examined a series of "polymerised" oils of various consistency, 1 to 5. No. 6 is a so-called "burnt thin". The table shows a continuous rise in the specific gravity, the oxy-acids, and the free fatty acids; first a rapid, then a slower decrease in the iodine number. That the saponification number first increases to fall later is due to the formation of volatile fatty acids which, later on, are volatilised at a greater heat.

PRINTING-INK VEHICLES. (LEEDS.)

	Density at 15° C.	Free Acid Calculated as Oleic Acid.	Saponification Value, KHO, mgs	Unsaponifiable Matter.	Oxidised Acids.	Iodine Value.
Raw linseed oil . .	0·9321	0·85	194·8	—	0·30	169·0
(1) Tint . . .	0·9584	1·46	197·5	—	1·50	113·2
(2) Thin . . .	0·9661	1·76	196·9	0·62	2·50	100·0
(3) Middle . . .	0 9721	1·71	197·5	0 85	4·20	91·6
(4) Strong . . .	0 9741	2·16	190·9	0·79	6·50	86·7
(5) Extra strong . .	0·9780	2·51	188·9	0·91	7·50	83·5
(6) Burnt thin . .	0·9675	6·93	195·5	1·35	0 85	92·7
Oxidised oil (weak) . .	1·03	18-28·4	221	0·81	42·82	58·8
" " (strong) .	1·05	18·49-28·9	22 ·5	0·97	44·19	53·5
Dried linseed oil . .	—	12·67	171·5	0·81	31·58	93·9

The unsaponifiable increases throughout being largest in amount in the burnt oil. Hydrocarbides are also produced, but to a very small extent. In the case of the mixed fatty acids the specific gravity and the iodine number generally run parallel with those of the glycerides. The great decrease in the iodine numbers of the linseed oil fatty acids by the above method of heating requires explanation; the evident shrinking of the mean molecular weight is probably due to hydrolytic products. It may be safely concluded from the above figures that the changes which occur during oil boiling are not due to retrograde saponification.

PRINTING-INK VEHICLES. (LEEDS.)

MIXED FATTY ACIDS.

	Density at 15° C.	Melting-point, Degrees C.	Solidifying-point, Degrees C.	Mean Combining Weight.	Saponification Value.	Iodine Value.
Raw linseed oil	0·923	24 26·5	—	286·5	195·8	145·6
(1) Tint	0·941	20·5	15	—	—	118·3
(2) Thin	0·949	22	18	—	—	108·8
(3) Medium	0·950	24	22	272·6	205·8	97·7
(4) Strong	0·953	25·5	24	270·1	207·7	87·3
(5) Extra strong .	0·955	27	23	269·8	207·9	90·8
(6) Burnt thin	—	23	19	—	—	99·3
Oxidised oil (weak) . .	—	28	26	241·4	232·4	63·2
,, ,, (strong) . .	—	27	25	212·5	231·3	60·6
Dried linseed oil	—	26	22	268·8	208·7	100·3

The Decreased Solubility of Thick Oil and Stand Oil in Alcohol.—H. Amsel found thick oil and stand oil less soluble in alcohol than raw oil. The test was made thus: 1 gramme of oil with 20 c.c. alcohol at summer temperature with frequent shaking; let stand 24 hours and then 10 c.c. filtered off. A pure linseed oil in this way gave 20 per cent. in solution. Four samples of thickened oil gave:—

TABLE SHOWING (*a*) SAPONIFICATION NUMBER, (*b*) IODINE NUMBER, AND (*c*) SOLUBILITY IN ALCOHOL OF FOUR SAMPLES OF THICKENED LINSEED OIL.

Number of Sample.	Saponification Number (*a*).	Iodine Number (*b*).	Solubility in Alcohol (*c*).
I.	195	94·4	18·5
II.	194	104	17·7
III.	209	—	9·2
IV.	192	—	6·0

The Increased Refraction of Heated Linseed Oil.—With stand oil and thickened oil there is a considerably higher refraction than for raw oil (80 to 81·5 at 25° C.).

REFRACTION OF STAND OIL AND THICKENED OIL.

	Butyrometric Refraction (25° C.).
Commercial stand oil	99·3
Thickened oil	92·9

The refraction increases with the temperature.

TABLE SHOWING INCREASED REFRACTION ON HEATED LINSEED OIL. (WEGER.)

	Butyrometric Refraction (25° C.).
Paint linseed oil	81·3
„ „ 6 hours heated to 150° C.	82·7
„ „ in litre flask heated to 280° C., mucilage freed	82·1
„ „ in litre flask heated to 315° C., mucilage freed	82·5
„ „ 40 hours heated to 180° to 190° C. .	90·9
„ „ 5 minutes to 300° C.	102·3

Lewkowitsch found during boiling of linseed oil that the hexabromide value rapidly decreased.

ANALYTICAL RESULTS OBTAINED BY LEWKOWITSCH IN THE EXAMINATION OF NINE SAMPLES OF LITHOGRAPHIC INK VEHICLES.[1]

	Density at 60° F.	Saponification Value	Iodine Value.	Hexabromides	Hehner Value.	Oxidised Fatty Acids.	Unsaponifiable Matter.
Raw linseed oil	0·9308	—	186·1	24·17	—	—	—
Linseed oil heated to 600° F.	0·9354	—	176·3	8·44	—	—	—
Thin varnish I.	0·9676	189·5	107·7	0 17	94·75	4·17	1·76
„ II.	0·9691	193·0	125·3	2 00	94·8	0·34	0·13
Medium I. .	0·9693	194·1	121·9	0·95	93·8	1·48	0·57
„ II. .	0·9703	190·5	126·5	0·0	—	1·53	1·8
Thick I. . .	0·9720	190·0	109·4	0·21	94·68	6·36	1·45
„ II. . .	0·9747	193·7	118 5	0·0	95·6	0·36	0·25
Burnt . .	0·9912	178·6	102·69	0 0	93·53	9·12	1·14

	Glycerine Obtained.	Acid Value.	Acetyl Value.	Iodine Value of Fatty Acids.	Liquid Fatty Acids.	Iodine Value of	
						Liquid Acids	Solid Acids.
Thin I. . .	9·71	6·09	6·5	114·74	39 31	131·29	106·2
Thick I. . .	9·17	5·12	16·5	113·53	32·31	130·4	106·43

Bearn analysed a series of printing-ink vehicles, which were prepared by heating linseed oil for a longer or shorter period at 300° C. and then "burnt".

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[1] Seven commercial samples were purchased and grouped according to their specific gravity. They gave the above results. The second samples, thin I. and thick I., were still further examined and the fatty acids extracted by Warrentrap's method.

TABLE SHOWING ANALYSIS OF A SERIES OF PRINTING-INK VEHICLES. (BEARN.)

Class of Vehicle.	d15	Free Fatty Acids, per Cent.	Unsaponifiable, per Cent.	Saponification Number.	Iodine Number.
Very thin stand oil	0·9152	3·19	0·35	186·5	157
Thin ,, ,,	0·9465	4·43	0·27	178·4	123·2
Middle ,, ,,	0·9574	5·25	0·31	183·8	115·4
Thick ,, ,,	0·9589	6·90	0·38	182·0	75·1
Very thick ,, ,,	0·9676	10·20	0·43	190·3	59·0

The chief point in this table is the unsaponifiable content. It falls slightly, to rise again, as during the boiling of the oil a portion of the original unsaponifiable is destroyed, but no fresh unsaponifiable matter is generated. *Tixier's Theory.*—Another anomalous result was obtained by A. Tixier. In his opinion linseed oil when heated alone, with exclusion of air, to about 300° C. (572° F.) loses little in weight, as the acid number and saponification number change little. However, the specific gravity rises above 1 and the oil solidifies. Tixier likens the process to an aldol condensation. the carboxyl groups remaining combined with glycerin, and as oxygen is not present, aldehyde groups cannot be produced. Moreover, a rearrangement of the hydrogen atoms can hardly occur without a reciprocal neutralisation of the double bonds. Such can be imagined in regard to the inner half of the molecule without "polymerisation". The increase in gravity and consistency favour a higher molecular weight.

Fokin's Experiments.—He, at one time, heats linseed oil in indifferent gases, CO_2, NH_3, at another time in sealed tubes to 250 to 300° C. (482 to 572° F.). The greater thickness obtained was traced back to "polymerisation". The polymerised glycerides can no longer be split up by lipase, and therefore the linolenic acid first polymerised may be isolated thus by the splitting process. In the determination of the freezing-point in benzol solution the molecular weight was found to be 2083, the original gave 0·832. The iodine number of the polymerised oil was about 141. In another research the linseed oil was heated for 50 hours in a sealed tube to 240 to 270° C. The molecular weight was 1913, the free fatty acids 32·6 per cent., iodine number 97·5. The lipase treated product was dissolved in petroleum ether and boiled 3 to 4 hours with bone char. The evaporated residue gave the molecular weight 564. Fokin therefore concludes that a depolymerisation of the bonds has occurred with the formation of di and monoglycerides. A third polymerisation product had the specific gravity 0·981, the molecular weight 1681, with 12·5 per cent. free fatty acids. By boiling the petroleum ether solution with bone char the molecular weight sank to 1239, and on further treatment with lipase to 803·5. In a fourth research the linseed oil was heated under a pressure of 90 to 118 atmospheres for 30 hours at 250 to 270° C. In spite of very great thickening the molecular weight only rose to 932·1. The question has been asked whether the thickening in this case was not due to physical causes. Free linoleic acid heated in a sealed tube doubled its molecular weight. It will be seen that the chemical action which occurs during the thickening of linseed oil by heat is by no means perfectly clear. On the technical side the question has been raised whether linseed oil bleached by sulphuric acid should be used for stand oil, as small traces of this acid in the refined oil impart a dark colour to the stand oil made from it. No drier is used in the preparation of printer's-ink vehicle, as it adheres so strongly to the type that it cannot be removed by hot lye. In the preparation of thick and stand oil, the oxygen of the air should not be utilised; heating in a vacuum is to be preferred. A. Genthe covers the oil with a movable sliding door. Finally, attempts have been made to remove the decomposition products in various ways. The chief ingredient of printing-ink vehicles is linseed oil after being boiled in a very special way; sometimes hemp oil is cheaper but worse smelling. A limpid, quick-drying oil, like that used in oil varnish-making got by boiling the oil at a heat below 220° C. (392° F.), is not wanted, but rather a viscous, partially resinified, partially decomposed oil such as is obtained by heating the oil a long way above its flash-point, i.e. above 250° C. (522° F.) (*vide infra*); such an oil leaves no greasy stain on paper.

Medium for Printing Ink and Lithographic Varnish Experiment.—Run about 4 ounces of linseed oil into an 8 ounce hard-glass flask. Weigh the flask without and with its contents. Place the flask on a ring (Fletcher's burner with foot) and heat very cautiously at first, using a low blue flame, then increase the heat gradually and watch the oil; it may possibly "spawn" or "break" owing to the presence of mucilage, but continue heating until, when at about 550° F. is reached, the oil takes fire at the mouth of the flask. Note the exact degrees Fah. Put out the gas then, extinguishing the flame from the linseed oil vapour by covering the mouth of the flask with not too large a piece of damp but not wet cloth. Then after the flame has been extinguished, remove the cloth, continue to heat the oil at 550° F. until it catches fire again; again extinguish, and again reheat until it takes fire once more. Put the gas out, let the oil cool on the Fletcher ring-burner on foot, and then re-weigh the flask and contents and note the loss in weight. Decant the clear oil from the deposited mucilage. This experiment teaches numerous lessons. The most important are: (1) The lesson conveyed, the loss in weight which is not all due to the burning of the oil. (2) The fact that the vapour given off by the decomposition of the oil is not a will-of-the-wisp even if it burns. (3) That vapour was being given off long before it caught fire, as it affected both eyes and nose previous to spontaneous ignition. (4) That it is not the vapour of the actual oil that catches fire but the vapour of the products into which the oil is so far resolved by the destructive-distillation it undergoes in heating from 60° F. to 550° F. Linseed oil so long as it remains linseed oil is not volatile. (5) That the fact that linseed oil when boiled at a high temperature gives off an inflammable vapour which takes fire spontaneously irrefutably demonstrates that the polymerisation theory as applied to oil boiling is, to say the least of it, unpardonable rank chemical heresy. (6) Note that the oil is so viscous that it does not readily flow from the flask, but that is not because the oil is polymerised; it is thickened partly by oxidation, partly by fractional distillation. (7) Note that it does not stain paper. In fact, the operator will in all probability have made an excellent sample of printing-ink vehicle, and that too in less than half an hour; and if the experimenter be a printer he can readily test the efficiency of his ink by rubbing it up with the requisite amount of lampblack. The printing and lithographic classes in technical institutes where the manufacture of painters' oils, colours, and varnishes are taught should be so far affiliated that both the lithographer and the printer, and apprentices in particular, should be taught by actual practice in the Oil and Colour Trade Laboratory how to make their own printing inks—i.e. how to incorporate lampblack, vermilion, and other pigments with the samples of printing-ink vehicle they make as in the experiment just described.

The reader, after performing the above experiment and testing his product in every way that may occur to him, will have a far better idea of what printing ink and its vehicles are than can be conveyed to him by any written description. If it be desired to make a larger quantity, then an enamelled iron pot may be used, and if opportunity occurs sufficient ink may be made to test it on the printing or lithographic machines in a printing and lithographic school.

Refining Raw Linseed Oil for Printing Ink.—In the experiment just described, we saw that the linseed oil " spawned " or " broke " or was liable to " spawn " or " break ". The object of refining is *inter alia* to eliminate this mucilage or " slime," as the Germans call it. Old tanked oil of prime quality is used to avoid the too dark colour and the not too pleasant smell of ordinary raw oil. It should be tanked a year or two so that all suspended impurities have completely separated out. Old tanked oil should be used, but it must still be specially refined by sulphuric acid. One great object of the sulphuric acid treatment is to bleach the oil, but unless the refiner be a man of experience the colour of that oil will in all probability be worse after treatment than it was before, although, as already mentioned, it can be got as near water-white as may be. The oil is mixed in a lead-lined vessel with 1 or 2 per cent. of sulphuric acid of about 103° Tw., specific gravity 1·515, and heated for several hours by means of a steam coil to a temperature of 90° C., taking care not to go beyond 100° C. The oil is then pumped into another tank to allow of the deposition of charred matter, and is afterwards decanted into a tank containing hot water, with which it is well washed, running off the wash water and agitating afresh, and so on until all trace of acid is removed. The oil is then boiled. As drying oils contain a certain quantity of fatty matter (palmitin) which does not dry and causes the printing ink to blot or blur, it has been recommended to eliminate it by adding to every 1000 parts of oil 1 or 2 parts of fuming nitric acid, which decomposes the palmitin into glycerine and palmitic acid, which may thus be precipitated as insoluble palmitate of lead or manganese. This process is an awkward and a dangerous one, not adopted to any extent, fuming nitric acid, in consequence of being easily decomposed, is by itself a dangerous substance; this danger is intensified to the highest degree when the acid is mixed with organic matter. Dangerous explosions may result and the oil take fire.

Description of Oil Boiling-pan in which Linseed Oil is "Boiled" so as to Convert it into a Printing-ink Vehicle.- If the injection of air be not resorted to by adopting one or other of the methods of air-blowing of oils, a pan capable of being heated over a naked fire must be used. In boiling oil by steam it is thickened by oxidation. In boiling over a naked fire it is thickened mainly by dry fractional distillation. In the latter case the oil is boiled either in a cylindrical copper pan, the lower half of which fits into the brickwork of the furnace, where it is kept in position by a collar which at the same time acts as a gutter to collect any overflow, or in a cast-iron enamelled pan. The pan is handled by an iron band encircling its top. Attached to the pan are strong lugs by which it is moved about safely. The capacity is 60 to 85 gallons. But in certain important factories in France, says Livache, the boiling is done in jacketed pans which do not cube less than 600 to 700 gallons; but in London that would be a small pan, where they boil oil in pans that take 10 tons at a time. In such cases a mechanical agitator is kept going during the boiling process, which may last two or three days, and with a 10-ton pan it is generally a horizontal helicoidal agitator like the propellor of a ship. But steam boiling must not be mixed up with fire boiling of oil. It has a special section to itself.

The Actual Process of Fire Boiling of Raw Linseed Oil so as to Convert it into a Printing-ink Vehicle.—The pan is filled half or at most three-quarters, a moderate heat applied so as to eliminate moisture. The slight ebullition caused thereby is not to be regarded as the "boiling" of the oil, although in former days it probably gave rise to the term, it is really the boiling of the water in the oil; when the oil "boils" quietly, i.e. when the water is expelled, the fire is urged until volatile, pungent, and disagreeable smelling products are given off. This takes place at a temperature of 250° to 270° C. (482° to 518° F.). In certain factories the workman satisfies himself as to this being the case by dipping in organic matter, such as a feather, for instance, which ought to inflame; or by projecting fine drops of water on to the surface of the oil, which as they fall decompose and scintillate, or, in other words, present, in consequence of the absorption of oxygen by the oil and the inflammation of the hydrogen, the appearance of stars. The fire is now carefully watched, for the oil may froth over or the vapours ignite. The frothing over is parried by adding a little cold oil. The oil becomes bright and more fluid at first, but, on being kept at this temperature for 1 or 2 hours, a brown red skin forms which is skimmed off as rapidly as possible. The temperature is now raised to 310° C. (590° F.), and kept at that for half an hour, watching the process with the greatest of care as the spontaneously inflammable vapours are very apt to catch fire. A well-fitting lid and wet cloths should be always at hand. The fire is let die down and the heat lowered to 260° C. (490° F.) to 270° C. (518° F.), when the pan is taken from the fire, covered with a lid and cooled. Certain makers, instead of cooling the oil after taking it from the furnace, set fire to the vapour it emits, and let it burn for a few minutes, as was done in the experiment previously described. They regard this treatment as indispensable to the production of a good article. Others contend that the same result is got by boiling the oil a little longer, which saves the appreciable loss of oil incurred by burning, and a much paler oil is obtained. Without expressing an opinion either way it may be well to point out that Savage was undoubtedly correct, because linseed oil when heated by a fire heat, and air not blown into it, does not thicken sufficiently until heated beyond the temperature at which the vapour given off by the linseed oil catches fire spontaneously. If the partial dry distillation of the linseed oil has not been carried far, one can readily imagine it will be as well for those vapours to be burnt off as to fall back into the oil. As to the oil darkening by burning, if that be so the darkening is so small as to be inappreciable. To heat linseed oil above the temperature at which its vapours catch fire in air, without spontaneous ignition, the air would have to be replaced by an inert gas, and that would spoil the oil. This attempt to belittle the burning process is only another absurd attempt by ultra-grandiose theorists absolutely ignorant of the rudiments of the subject they pretend to teach in order to prove the rule-of-thumb man wrong. It is not a question of whether inflaming the oil is a necessity; but who and what is to prevent linseed oil from inflaming when its temperature is raised far above its flash-point, above that at which it spontaneously ignites. This the author (McIntosh) found it to do at the orifice in a medium narrow necked 6 to 8-oz. flask, an ordinary necked 8-oz. flask in fact, when the oil registered a temperature of 525° F.

"*String*" *Test.*—The exact moment when the pan ought to be removed from the fire is determined by the "string" test. A small sample of oil is taken from the pan on an iron spatula, and cooled rapidly. A drop is taken and pressed between the finger and thumb which are then gradually drawn apart as far as possible. If the oil is sufficiently boiled, the thread joining the finger and thumb together stretches 1 to 2 inches without breaking.

Properties of Good Printing Ink.—Good printing ink has the requisite body of a pale, bright yellow colour—not deep yellow or brown—and is not cloudy from matters in suspension. It is very evident that the body of the oil will depend upon the purpose for which it is intended. For printing books and lithographic work an oil having a good body is required, whilst for newspaper printing a soft, almost fluid oil is used. According to Villon, who made an elaborate study of printing ink, five kinds of oil of different body or consistency are in the market, viz.:—

(1) Extra strong, (2) strong, (3) medium, (4) weak-bodied oils, and (5) drying oil. The strong-bodied oil (2) is used in summer for very particular work with the hand press. The medium oil (3) is used in ordinary weather. The weak-bodied oil (4) is used in winter with the mechanical press, whilst the drying oil (5) is used to prevent the formation of the oily ring around the letters.

Driers and Extra Strong-bodied Oil.—Usually no driers are used, because oil boiled with driers would clog the type, and could not be removed even when washed with a hot alkaline solution. There is sometimes, however, an advantage in using such an oil, and to meet this want the oils known as "extra strong" and "drying" oils are manufactured.

The "extra strong-bodied" oil is made by boiling with lead salts, and the "drying" oil by boiling with an oxide or salt of manganese.

Strong-bodied oil (2) (*huile forte*) is prepared by setting fire to the oil, letting it burn for five minutes, and stirring several times. The flames are put out and the oil again set on fire, twice at least, and sometimes four times. The cooled oil strings like treacle. The "fatty" oil is made by shortening the burning process, and is intermediate between the other two. Nowadays a process similar to that used in making ordinary printing ink is adopted. The removal of grease by onions or bread is then effected by nitric acid, as previously indicated, or by magnesia. This latter, which is extensively used in England, consists in adding 2 per cent. of magnesia, boiling for an hour, and decanting. The oil is then run into a pan capable of holding 42 gallons, and gradually heated to 182° C. (327·6° F.), 3 hours being occupied in attaining this point. About 1¼ lb. of finely ground bichromate of potash is then added, and the temperature is raised to 300° C. (572° F.), stopping the frothing of the oil by adding a little cold oil, then it is kept for half an hour at a temperature between 315° and 320° C. (599° to 608° F.), after 1¼ lb. of Prussian blue have been slowly added. "Strong-bodied" oil is thus obtained, intermediate between the other two. To make "fatty" oil, the oil is only heated for 5 minutes to 300° to 305° C. (572° to 581° F.). With "pale" oil the heat does not rise above 275° C. (527° F.), which is maintained a quarter to half an hour according to the object in view.

In reference to certain so-called "rule-of-thumb" practices in connection with this process, it is necessary to point out that the badly informed theorist is unaware that the onion contains sulphur in organic combination, in such combination in fact that it readily yields itself to the partial vulcanisation of the oil, and contributes to the drying, thus acting beneficially on oils intended for certain purposes, more especially for printing ink. Nor is there any reason why bread should not accumulate palmitin in its pores. Why should not bread act in much the same way as a "hygroscopic" substance to palmitin, the most viscous of the ingredients of linseed oil? Those who in season and out of season would air their superior knowledge should take care that they are not the persons whose lack of true scientific knowledge is most palpably in evidence.

The highly complex organic sulphur compounds elaborated in the onion act chemically on the oil to form sulphur compounds; they partially vulcanise it just as litharge is reduced to metallic lead and parts with its oxygen to the oil. In like manner the "drying oil" is obtained by heating for 15 hours at 275° C. oil to which 0·05 per cent. of the hydrated oxide of manganese has been added, or by boiling oil for 24 hours at 300° C. (572° F.), with 0·5 per cent. of black oxide of manganese. If borate of manganese be used 4 lb. of this salt are beaten up with 25 lb. of linseed oil, and the homogeneous mixture run into 200 lb. of linseed oil, and the whole heated for ½ hour at 250° C. (482° F.), or ¼ hour at 316° C. (600° F.). This should give a 2 per cent. solution of borate of manganese in the bulk of the oil. Some manufacturers are said to add 2½ per cent. of oxalate of manganese ($MnC_2O_4H_2O$) whilst applying heat for 3 hours at 150° C. (302° F.) to 160° C. (320° F.)—but that is far too low a heat to dissolve that drier—or simply add a manganese soap dissolved in coal-tar naphtha petroleum ether, turps or white spirit. Turps is a better solvent for linoleates and rosinates than white spirit.

Use of Rosin.—Black rosin is an important article in the composition of good ink; as by melting it in the oil, when that ingredient is sufficiently boiled and burnt,[1] the two combine, and form a compound approximating to a natural balsam, like that of Canada, which is itself one of the best varnishes that can be used for printing ink. When great body is required without having recourse to prolonged boiling, rosin is added. Rosin is, in fact, extensively used in the making of printing ink. With ordinary black ink, common rosin is used, but for fine, coloured inks, pale American rosin is employed.

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[1] Note these words, because they inculcate a principle which is this, that rosin when heated to a certain temperature, that is, subjected more or less to dry distillation for a certain time, ceases to be rosin and is changed to a new body altogether more fit for the duties it is called on to perform.

The rosin is melted, filtered to eliminate rubbish, and added to the oil during cooking or boiling. When very high-class inks are required for jobs to be executed in an especially neat and delicate manner, balsam of Peru, Canada balsam, or copaiba balsam are used instead of rosin.

Copaiba balsam is said to produce a good extemporaneous ink when mixed with the proper quantity of soap and pigment.

Balsam of capivi, mixed by a stone and a muller, with a due proportion of soap and pigment, forms an extemporaneous ink, which the printer may employ very advantageously when he wishes to execute a job in a peculiarly neat manner. Canada balsam does not answer quite so well.

Soap.—This is a most important ingredient in printers' ink, which is not even mentioned in any of the recipes prior to that in the "Encyclopædia Britannica". For want of soap, ink accumulates upon the face of the types, so completely as to clog them up after comparatively few impressions have been taken; it will not wash off without alkaline lye and it skins over very soon in the pot. A certain quantity of hard soap is added to the oil during boiling, which imparts suppleness, but its principal object is really to facilitate the cleansing of the type, enabling this to be done with a brush. The soap ought to be perfectly dry, that is, to have been left for a long time in thin slices at 100° C. (212° F.), until it ceases to lose weight. Ordinary yellow rosin soap is used for common black ink, but for fine inks, for light and delicate shades of colour, white curd soap is used. Too large a proportion of soap retards drying and gives rise to irregular printing. The printing-ink maker should only use as much soap and no more as will cause the ink to work clean and without clogging the type. The following are a few examples with quantities:—

	Best. lb.	Medium. lb.	Ordinary. lb.
Boiled oil	100	100	100
Rosin	25	50	75
Soap	4	6	8
Drying oil	6	9	12

For ordinary, such as newspaper, work great economy is necessary, hence in place of boiled oil there has been used a mixture of raw oil and thickened turpentine; the quantity of rosin is increased and the requisite fluidity obtained by the addition of rosin oil.

The proportions given by Andés are as follows, according to the amount of body required:—

	lb.	lb.	lb.
Raw linseed oil	140	110	90
Rosin oil	240	240	240
Rosin	210	210	210
„ (i.e. yellow) soap	5	5	5
Thickened turpentine	5	5	5

Common inks are made very cheaply by replacing linseed oil by rosin oil, for which purpose the following recipes have been given:—

	lb.	lb.
Rosin oil	1000	1000
Rosin	400	780
„ soap	100	780
Ordinary soap	100	180

GOYNEAU'S PRINTING INK.

	lb.	lb.	lb.
Linseed oil	979	400	980
Litharge	125	60	122
Rosin	735	380	980
Syrup	245	980	958

Method of Adding Rosin and Soap to the Burnt Oil and Subsequent Reheating of the Latter.—After the smoke begins to rise from the boiling oil, a bit of burning paper stuck in the cleft end of a long stick should be applied to the surface, to set it on fire, as soon as the vapour will burn; and the flame should be allowed to continue (the pot being meanwhile removed from over the fire, or the fire taken from under the pot), till a sample of the varnish, cooled upon a palette-knife, draws out into strings of about ½ inch long between the fingers. To 6 quarts of linseed oil thus treated 6 lb. of rosin should be gradually added, as soon as the froth of the ebullition has subsided. Whenever the rosin is dissolved, 1¾ lb. of dry brown soap, of the best quality, cut into slices, is to be introduced cautiously, for its water of combination causes a violent intumescence. Both the rosin and soap should be well stirred with the spatula. The pot is to be now set upon the fire, in order to complete the combination of all the constituents.

Put next of well-ground indigo and Prussian blue, each 2½ oz., into an earthen pan, sufficiently large to hold all the ink, along with 4 lb. of the best mineral lamp-black, and 3½ lb. of good vegetable lamp-black; then add the warm varnish by slow degrees, carefully stirring, to produce a perfect incorporation of all the ingredients. This mixture is next to be subjected to a mill, or slab and muller, till it be formed into a smooth uniform paste.

One lb. of a superfine printing ink may be made by the following recipe of Mr. Savage: Balsam of capivi, 9 oz.; lamp-black, 3 oz.; indigo and Prussian blue, together, p. æq. 1¼ oz.; Indian red, ¾ oz.; turpentine (yellow) soap, dry, 3 oz. This mixture is to be ground upon a slab, with a muller, to an impalpable smoothness. The pigments used for coloured printing inks are—carmine, lakes, vermilion, red lead, Indian red, Venetian red, chrome yellow, chrome red or orange, burnt *terra di Sienna*, gall-stone, Roman ochre, yellow ochre, verdigris, blues and yellows mixed for greens, indigo, Prussian blue, Antwerp blue, lustre, umber, sepia, browns mixed with Venetian red, etc.

Indigo alone, or with an equal weight of Prussian blue, added in small proportion, takes off the brown tone of certain lamp-black inks. Mr. Savage recommends a little Indian red to be ground in with the indigo and Prussian blue, to give a rich tone to the black ink.

The following tables give various kinds of printing-ink vehicles which find employment in this branch of industry:—

PRINTING-INK VEHICLES.

	I.	II.
	lb.	lb.
1. Venice turpentine	60	9
2. Olein	30	4
3. Soft soap	80	10
4. Lamp-black	50	4 or more
5. Prussian blue	40	—
6. Oleic acid	20	—
7. Water	20	—

Mix 1, 2, and 3 with aid of heat. Stir in 4 after sifting finely, then incorporate with I. the solution of 5, 6, 7. The 40 lb. of Prussian blue may be replaced by 20 of indigo carmine first rubbed up with water. It is claimed for II. that it can be removed from old printed paper and renders printers' lye unnecessary.

PRINTING-INK VEHICLES.

	Thick Boiled Oil.	Rosin.	Rosin Oil.	Rosin Soap.	Linseed Oil Heated to 30° C.	Turps.	Raw Oil.
Thick I*ma*	150	75	75	9	12	—	—
" II*a*	150	150	150	15	12	—	—
" III*a*	150	220	150	21	12	—	—
Medium I*ma*	150	75	150	9	12	—	—
" II*a*	150	150	150	15	18	—	—
" III*a*	150	150	150	20	27	—	—
Thin I*ma*	150	75	150	9	21	—	—
" II*a*	150	150	150	15	27	—	—
" III*a*	150	226	150	21	36	—	—
Thick I*ma*	—	210	240	5	—	5	87
" II*a*	—	210	275	7	—	7	50
Medium I*a*	—	105	240	5	—	5	210
" II*a*	—	105	300	7	—	7	150
Thin I*a*	—	130	240	5	—	5	160
" II*a*	—	150	345	7	—	7	110

PRINTING-INK VEHICLES.

	Thin.	Medium.	Thick.
	lb.	lb.	lb.
Rosin	25-75	25-50	25-75
,, oil	50	50	50
Boiled oil	50	50	50
Rosin soap	3-7	3-7	3-7
Thin-boiled oil	7-12	4-9	—

	Thin, with Boiled Oil.						Medium, with Boiled Oil.		Thick, with Boiled Oil.						
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
Rosin oil	50	50	50	—	—	—	—	—	—	—	—	—	50	50	50
,,	25	50	75	125	250	384	250	125	384	125	250	85	50	50	50
Boiled oil	50	50	5	500	600	600	600	500	600	500	500	13	50	50	75
Rosin soap	3	5	7	15	50	77	50	15	35	15	35	—	3	5	7
Boiled oil	7	9	12	—	—	—	—	—	—	—	—	—	—	—	—
Linseed oil heated to 30° C.	—	—	—	—	—	—	30	20	45	35	60	—	—	—	—

	Thin.			Medium.			Thick.		
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
Rosin	25	25	25	50	50	50	77	77	77
Boiled oil	100	100	100	100	100	100	100	100	100
Rosin soap	3	3	3	10	10	10	7	7	7
Weak-boiled oil	7	4	—	9	6	—	12	9	—

	Thin.		Medium.		Thick.	
	lb.	lb.	lb.	lb.	lb.	lb.
Rosin oil	96	95	240	80	240	80
Raw linseed oil	84	—	210	—	210	—
Rosin soap	2	7	5	70	5	7
Thick turpentine	2	—	5	—	5	—
Rosin	—	100	—	100	—	100
Boiled oil	52	35	1000	3500	87	25

PRATT'S ORIGINAL ROSIN OIL PRINTING-INK VEHICLE.

	lb.	lb.
Rosin oil	20	50
Rosin	8	39
Yellow soap	2	9

PRINTERS' INKS FOR VARIOUS PURPOSES.

Use.	Rotary Machines.						Newspaper.		Book.			Illustration.		
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
Vehicle . .	70	72	72	72	74	74	78	76	77	79	80	78	78	78
Lamp-black .	30	28	28	28	26	26	22	24	23	21	20	20	19	19
Prussian blue .	—	—	—	—	—	—	—	—	—	—	—	2	2	1
Indigo . .	—	—	—	—	—	—	—	—	—	—	—	—	1	—
Chinese blue .	—	—	—	—	—	—	—	—	—	—	—	—	—	2

	Common Black.	Rotary Soft.	Jobbing.
	lb.	lb.	lb.
Paraffin Oil . .	25	25	25
Rosin . . .	45	40	—
Lamp-black . .	15	15	15
Dammar . . .	—	—	45

Rosin of different grades may be used, or Burgundy pitch. Paraffin oil may be replaced by rosin; the proportion of lamp-black is adjusted accordingly. Other pigments in suitable proportion may be substituted for lamp-black.

GUNTHER'S PRINTING INK.

	lb.	lb.
Heavy tar oil	45	28
Pitch or asphaltum	40	40
Rosin pitch soap	12	24
Fish oil	5-8	—
Spirit soluble aniline dye in powder .	3-15	8

The heavy tar oil is first acted on by chlorine at 212° F., or is heated with nitric acid to deodorise it. The oil is then boiled with 5 to 10 per cent. of chloride of copper, heated to remove free acid, and then dissolved in warm water or stirred into the oil to give the oil a brownish-black colour, and thus reduce the aniline dye to a minimum—⅛ per cent. is then sufficient. The oil thus treated can be used as a stamping ink for post-office work without any addition.

Blue-black Ink.—A little indigo blue is also added to the hot oil to impart lustre, or 1 per cent. of Prussian blue may be added as the oil commences to boil, which, as it dissolves, yields a beautiful blue-black and imparts drying properties.

Generally in the actual manufacture of the ink, the boiled oil is moderately heated with the simple addition of rosin and soap alone until the mass becomes tranquil and homogeneous; the colour is then added and ground in the mill until perfectly cold. Another process consists in melting the rosin until destructive distillation commences, then to add soap in slices, afterwards the boiled oil. Heat is now applied more strongly, so as to increase the fluidity of the mass, then the colour is added, and the whole run into a receiver, from whence it passes to the mill while still hot. The nature and the quantity of the colouring matter depend upon the consistency of the oil and the object in view, but heavy, dense mineral colours should, as far as possible, be excluded, using in preference fine colours, free from coarse particles, which give a more homogeneous and impalpable ink.

Printing ink ought to satisfy several tests. (*a*) It ought to be perfectly homogeneous, for the least particle of extraneous matter (grit, etc.) will cause a blot in the printing; (*b*) it should not alter when exposed to the air in bulk for a long time, but when spread in a thin layer it should dry very quickly, without, however, commencing to do so on the type, from which it should be easily removed by washing; (*c*) the colour of dry printing ink should be rich and brilliant; (*d*) it should not penetrate the paper too deeply but deep enough to prevent it being detached from the surface; (*e*) finally, it ought to have no bad smell. The proportions of different substances entering into the composition of printing ink vary much. They may, however, be reduced to three types:—

De Luxe Illustrations, Ink for:—

	lb.
Thin oil	1000
Thick oil	250
Lamp-black	500
Prussian blue	50
Rosin (yellow) soap	25

Prussian blue is first added to thin oil in a pan fitted with a mechanical agitator, and heated to 100° C. (212° F.) by a steam jacket. The heat is raised to 150° C. (302° F.), and the rosin soap is mixed with continual stirring. It is only when perfectly cold that the black is introduced into the mixture, then the thick oil. The whole is then passed through rollers. Small quantities may be ground in a mortar worked by power. [By using carbon gas-black instead of "lamp"-black a superior jet black is obtained.]

Black Ink for Engraving Purposes.—Villon's researches resulted in his selection of the following formula as yielding a very black ink for engraving purposes, without reddish reflex, and of irreproachable composition, which keeps well, and each of the ingredients of which plays an important part:—

	lb.
Huile claire (pale limpid oil)	1000
„ *forte* (strong-bodied oil)	200
Carnauba wax	25
Paraffin	35
Yellow soap (rosin)	25
Paris violet	0·5
Prussian blue	40
Cork black	100
Blood black	50
Winelees black	200
Ivory black	150

Numerous other substances are also used to impart consistency and unctuosity, such as Canada balsam, ozokerit, asphaltum, stearic acid. It is for each manufacturer to select those materials best adapted for the object in view. The retention of the copper lustre of Prussian blue in the matter printed from an ink made from that pigment is a subject which has interested and engaged the attention of not a few. Some claim to have succeeded by the use of lard, etc. But the copper bronze reflex of modern printed matter is undoubtedly due to nigrosine black and aniline blues. With the use of these the difficulty is not in retaining the bronze, it is in eliminating it.

In copper-plate and steel-plate engraving (*taille douce*) an engraved plate of copper or steel, the engraving being hollow, is covered by an ink with a prepared oil vehicle, then energetically cleansed, so as to leave only the ink in the hollows of the engraving. A sheet of moist paper is then pressed strongly against the surface of the plate, so as to force the paper into the hollows and there become inked. That is the principle of steel and copper-plate engraving. The ink is similar to that used in ordinary printing ink, but it must not be too viscous. It must be readily detached from the delicate touches, *finisses*, of the engraving. Lamp-black is, therefore, replaced by special blacks, vine black, Frankfort black, which yield less adherent mixtures with boiled oil.

Villon's Ink for Steel Engravings.—The vehicle for this ink, according to Villon, who made a special study of ink for steel engravings, is prepared like ordinary printing-ink vehicle, the only difference being that it is boiled a little longer. Old tanked linseed oil, i.e. well-aged oil, is the oil employed, or, better still, walnut oil; but this latter oil is never used alone, a little linseed oil, varying from 12 to 50 per cent., according to the quality of ink desired, being always added to give it more viscosity. The boiling process, although an old one, is that still used. It consists in heating 5 gallons of oil in a pot until it takes fire or gives off white vapours which are set on fire. It is left to burn for 5 minutes, taken off the fire, and placed on a furnace filled with hot ashes, where it is let burn a few minutes longer. A piece of stale bread, held by a pair of pliers, is dipped into the oil until it reddens, without, however, charring; it is replaced by a second slice, and that by a third—the bread is sometimes replaced by peeled onions.

Vehicle for De Luxe Printing and Illustrations.—Finely ground pigments are used for *de luxe* illustrations and *de luxe* printing; the vehicles used are thick linseed oil, strongly boiled (double boiled) linseed oil, with the addition of copaiba balsam, Venice turpentine, dammar varnish, copal varnish, amber varnish, liquid driers, etc. Recipes for the making of preparations for the above purpose, intended to give a lustre which linseed oil alone cannot give, are

	I. lb.
Dammar varnish	60
Venetian turpentine	30
Canada balsam	15
Copal varnish	8
Bergamot oil	8

	II. lb.	III. lb.
Copaiba balsam	24	17
Linseed oil	17	8
Rosin	37	23
Amydaloid benzoin	1	0·60
Balsam of Tolu	0·64	0·4

The Printers' Ink Vehicle for Gold Printing is a very tacky one, which is used as an undercoating when gold bronze is applied. To 70 parts of such an undercoat, 30 parts of flesh-coloured ochre are added, and 50 parts medium thick varnish, and 20 parts Canada balsam. F. Hallmeyer used 4 parts medium strong vehicle, 2 parts of wax, and 1 part Venetian turpentine. Finely ground raw sienna, free from the least trace of grit, is added when undercoats for bronze printing are being used. The addition of wax greatly increases the adhesion of the ink, and it is advisable to make sure that wax has been added. A vehicle for bronze gold printing was patented by Hinzelman. He used 5 lb. zinc white, ground in 22 lb. linseed oil, then he added to the mixture of the two, 22 lb. of gold bronze printing-ink vehicle, 3 lb. of Venetian turpentine, 3 lb. of wax, and 2½ lb. asphaltum, and then heated the mixture until of the right consistency.

Printing Gold Bronze on Silk.—The silk is impregnated with a thin solution of water-glass. A small quantity of raw sienna is rubbed up with No. 3 vehicle, and then added to a composition vehicle of 10 parts of wax, 10 parts of Venetian turpentine, 25 parts of varnish, vehicle No. 2, and 5 parts boiled linseed oil.

For Brilliant Printing and also for Printing by Dusting on Wool.—A composition is made of a solution of rosin, boiled oil, liquid drier, copal varnish, and Venice turpentine.

Lustrous Printing Ink.—This effect is due to the pigment as a whole or in part, shining through the vehicle which exhibits a lustrous coating. The lustre can only be produced by the first printing, and then only on strongly satined and well-sized paper, otherwise the upper surface of the printed varnish layer will sink. A more decided lustre may be obtained by the addition of certain ingredients to the vehicle. Now such an addition is more or less to be feared, as some of the fatty lustrous ingredients do not adhere to pigments very well.

Recipe for Lustrous Vehicle.—(1) 2 parts mastic, 2 parts sandarac, 2 parts thick varnish vehicle are melted, and when cold 2 parts Venice turpentine and 3 parts liquid drier are added.

(2) 1 part dammar varnish, 1 part drier, 1 part thick oil are heated with 10 per cent. of mastic and diluted with thin vehicle.

N.B.—Copal oil varnish is made from fused hard copal, also from soft copal, then the fused resins are added to a small portion of linseed oil, previously heated. If lumps are formed after each addition, the mass is stirred and no thinner added until complete solution is effected. Zohmann gives the following instructions for making such a varnish: 6 lb. fused copal, 14 parts raw linseed oil or boiled linseed oil, 8 parts turps. But see vol. iii.

At the present day, especially for book-printing and lithography, lakes from coal-tar colours are quite indispensable.

CHAPTER XI.

THE TECHNICAL CHEMISTRY OF LINSEED OIL AND THE MANUFACTURE OF BLOWN OILS AND LINOLEUM.

It has been seen that when linseed oil is stored with complete exclusion of air no chemical change occurs further than a slight increase in the acid number, but when linseed oil is heated with exclusion of air, besides a marked increase in the acidity of the oil, there is a decided increase in the specific gravity, whilst, on the other hand, the iodine number is correspondingly lowered. It is well known that the great oxidation which linseed oil undergoes during storage with access of air is due to the absorption of oxygen and that this autoxidation which occurs between the oil and the air is slow, but is accelerated by heat. The changes in the organoleptic and physical properties of the oil are very similar to those induced by heating oil with exclusion of air. The body, consistence, or viscosity of the oil is increased, and it may safely be said that all raw linseed oils with a specific gravity above 0·933 are more or less oxidised by absorption of oxygen from the air. The index of refraction increases whilst the calorific intensity diminishes. So-called polymerised oils or oils thickened by heating without access of air and oxidised oils may be differentiated from each other by the fact that the "polymerised" oils may be drawn out into long strings, whilst the oils thickened by oxidation give an emulsion with water. Moreover, the chemical changes which linseed oil undergoes during heating with access of air are to some extent similar to those which occur during heating with exclusion of air: an increase in the acidity (acid number) and a lowering of the iodine number. Parallel with this sinking of the iodine number is an increase in the percentage of oxyacids. Partially oxidised linseed oil is not completely soluble in petroleum ether. Moreover, the fatty acids separated from the saponified product from such an oil are only partially soluble therein and the percentage of oxyacids insoluble in petroleum ether is greater, the longer the duration of the oxidation of the oil.

Cloez's Early Experiments on Increase in Weight of Linseed Oil on Drying and the Nature of the Volatile Compounds Evolved.—Before Mulder's time, Cloez had examined the action of the oxygen of the air on vegetable oils. He exposed 10 grammes of oil to the air, in an iron basin, and left it so until the increase in weight became constant. Such a point he found in all oils, and wished to draw therefrom a broad distinction between drying and non-drying oils, which was not adopted. The 10 grammes of oil had, in 18 months, absorbed 0·703 grammes. Both the original and the oxidised oils were subjected to combustion, which gave the following results :—

	Per Cent.	Oxidised Oil, 100 Parts.	Oxidised Oils, 107·3 Parts.	Difference.
C	77·6	67·5	72·3	- 5·3
H	11·3	9·9	10·6	- 0·7
O	11·1	22·6	24·1	+ 13·0

Acrolein the Chief Volatile Compound from Linseed Oil.—Oxygen was absorbed,, C and H split off. Cloez found little CO_2 and H_2O amongst the fluid oxidation products. He believed they consisted chiefly of acrolein. The paper with which the basin, used in the experiment, was covered, had become yellow, and Cloez attributed the yellowing to acrolein, and the yellowing of printed books to the same cause, as printing-ink blacks contained linseed oil. But this yellowing is due to the linseed oil dissolving the tar of the lamp-black. Mulder regarded Cloez's differentiation between drying and non-drying oils as correct only from a quantitative point of view, in which the drying oils, as a whole, on complete oxidation pass into a solid body whilst the non-drying oils absorb much less oxygen and only leave a solid body in small quantity. Mulder recognised, and quite correctly so, that during Cloez's experiments the oxidation of the inner linseed oil could only have been partial, as a skin was formed on the surface, which protected the oil underneath from the oxygen of the air. Mulder accentuates, in his book, again and again that the linseed oil be exposed to the air in a thin film.

Kissling's Experiments.—However, R. Kissling, 25 years later, used a similar method to Cloez. He placed 10 grammes of oil in a watch glass of 35 sq. centimetres in surface, and found the oxygen absorption in 25 days 5·13 per cent., reaching a maximum of 5·7 in 42 days. Kissling thus committed the same error as Cloez. According to Mulder the reaction is unfinished and could never come to an end, as the skin formed protects the lower layer. There is thus quite unchanged linseed oil, solidified oil, with slightly oxidised oil, and still untouched oil underneath, and still quite unchanged oil on the bottom of the watch glass. In what is presumably a separate experiment, Kissling spread 10 grammes of several oils over 35 sq. centimetres and exposed the same for 10 days at the ordinary temperature, with the following results :—

Oil.	Increase in Weight per Cent. at Ordinary Temperature.	Oil.	Increase in Weight per Cent. at Ordinary Temperature.
Olive. . . .	0·0	Cotton-seed . .	0·545
Rape (crude) . .	0·05	Raw linseed . .	1·130
„ (refined) . .	0·000	Boiled „ . .	3·400
Neatsfoot (refined) .	0·065	Triolein . . .	0·0

This layer was far too thick.

Even after 25 days the linseed oil showed an increase in weight of only 5·13 per cent. when a skin began to form, and in 42 days the maximum of 5·7 was reached. Kissling evidently committed the same error as Mulder accused Cloez of doing, that is experimenting on far too thick films. With thick films the reaction never comes to an end—the product is quite unfinished, the circumambient skin floating on the liquid layer beneath effectually isolates it from the air which alone can complete the reaction. There is, therefore, completely oxidised solid oil on the top with still almost unchanged oil at the bottom of the watch glass. The study of the oxidation of linseed oil was begun long ago by Mulder, and Hazura's researches gave it a fresh impulse. Bauer and Hazura tested two samples of linseed oil which had been kept for two years in loosely corked bottles and found the acid numbers had risen to 8·9 and 12·1.

Thompson and Ballantyne left linseed oil in an open vessel with frequent stirring for six months and found the specific gravity had risen from 0·9331 to 0·9385 and the iodine number had sunk from 173·5 to 166·2.

Fahrion uses the result obtained by the estimation of the oxyacids to ascertain the degree of oxidation of the oil. In a more than one-year old sample of linseed oil occasionally warmed but kept in a glass vessel that was not quite full and frequently opened to draw out samples, the iodine number was still 153 and the oxyacids 6·5 per cent. A sample of this oil was heated in an open porcelain dish for 4 hours at 110° C.; the iodine number sank to 136·1 and the oxyacids had risen to 11 per cent.

Sherman and Snell found a decrease in the calorific intensity of linseed oil stored with access of air, whilst the specific gravity had increased so that the products of the two figures were constant. In the thick oil it came out as 8·6 to 8·8.

TABLE SHOWING CHEMICAL AND PHYSICAL CHANGES LINSEED OIL UNDERGOES ON STORING WITH ACCESS OF AIR, INTER ALIA IN CALORIFIC INTENSITY. (SHERMAN AND SNELL.)

	Raw Linseed Oil of 1900.	Raw Linseed Oil of 1898.	Raw Linseed Oil Several Years Old.
d 15·5° C. . . .	0·934	0·938	0·947
Iodine number . .	182·4	175·9	156·7
Free fatty acids, per cent.	4·3	1·2	5·3
Heat of combustion, constant volume, calories per gramme. . .	9304	9379	9215
Heat of combustion, constant pressure . .	9379	9394	9230

Sherman and Falk left linseed oil in uncorked flasks protected from dust, with occasional shaking, but exposed to the air for a long time.

TABLE SHOWING CHANGES LINSEED OIL UNDERGOES ON STORING WITH ACCESS OF AIR. (SHERMAN AND FALK.)

	Fresh Oil.	After 4 Months.	After 8 Months.
d 15·5 C.	0·934	0·942	0·966
Iodine number . . .	178	165·8	139·4
Free fatty acids, per cent. .	1·3	2·2	4·4
Hexabromide number . .	31·3	—	32·8
Reichert Meisl number . .	0·49	1·10	2·64

Here the slight increase in the hexabromide number is surprising: a decrease was to be expected, as oxygen is fixed by the double bonds of linolenic acid. With non-drying oils the change was steadier. An increase in the gravity of 0·001 corresponded with a sinking of the iodine number of 0·8. With linseed oil water was given off. Thoms and Tendler have shown that in the autoxidation of linseed oil, the unsaponifiable number is not increased; 20 grammes of linseed oil were left in an uncovered glass dish for 40 days, exposed to air and light. The unsaponifiable was (*a*) before, 1·05; (*b*) after, 0·98 per cent.; heated for 48 hours in same dish to 100° C., 0·86 per cent. A La Plata raw oil with 0·98 unsaponifiable was left in a beaker three-quarters full, covered with filter paper, for 3 months in clear daylight. The unsaponifiable then was 0·95, its iodine number sank from 97·1 to 86·0. Linseed oil from Memel seed was exposed in a thin layer in clear daylight in a loosely covered glass dish until it was completely dry. The unsaponifiable was before 1·09, after 1·03 per cent. The iodine number before 92·3, after 55·8.

Volatile Products Evolved from Linseed Oil Dried at a Low Temperature.—Lidoff and Fokin found that when linseed oil is dried at a somewhat low temperature, besides CO and CO_2 hydrocarbides are evolved in variable quantities. The oxidation of linseed oil in the air at the ordinary temperature is a long affair, so far as the thin film is concerned.

Henrique's Researches on the Drying Capacity of Ethyl Linoleate.—In this connection comes the linseed oil ethyl ester, i.e. a mixture of the ethyl esters, of the mixed fatty acids of linseed oil, otherwise ethyl linoleate, which has a deal higher oxidation capacity, as the triglycerides are of much lower molecular weight. Henrique's ethyl "linoleate" is a pale yellow thin fluid oil, which in large quantities is extraordinarily unstable. Freshly prepared, it is readily soluble in petroleum ether. Exposed to air, it thickens rapidly, becoming more and more insoluble in petroleum ether. The autoxidation gave the following results:—

TABLE SHOWING THE DRYING CAPACITY OF ETHYL LINOLEATE.

Ethyl Linoleate.	Acid No.	Saponification No.	Iodine No.	Acetyl No.
2 days old	0	181·7	170·4	42·5
3 weeks old	4·2	213·6	—	85·1
6 " "	—	220·4	83·5	104·9
6 " " petroleum ether insoluble portion . .	—	271·9	36·1	—

Oxidation of the Linseed Oil in Linseed Oilcakes.—Here the remarkable rise of the saponification number is noticeable, which later on will be found in very highly oxidised oils. Now the thin film of linseed oil is resorted to, so that the particles of the oil be spread or subdivided over a substance with a great surface. Such a body is found in crushed linseed and linseed cake. The oils in these bodies with access of air rapidly oxidise. Nordlinger found in technically expressed linseed oil 0·2 to 2·1, on an average 0·8 per cent. free fatty acids. In several linseed cakes he found 6·8 to 10·8 per cent., average 8·8 per cent oil, and therein 4·0 to 15·5 per cent., on an average 9·75 per cent. free fatty acids. In extracting linseed oilcakes with ether less oil is obtained when the cakes are first dried at 100° C. Two air-dried oilcakes gave 8·0 and 10·3, but after 6 hours' heating to 100° C. only 3·7 and 7·7 of oil. But the loss of oil by volatilisation is negligible, such results are due to oxidation. Mastbaum concludes that the lowering of the iodine number of the oil from linseed oilcake is the first outcome of oxidation in his accentuation of Ketel and Antusch's results. Mitarewski found an increase in free and volatile, also a decrease in unsaturated fatty acids in the oil from linseed oilcake. He believes, however, that glycerine is partly split off by micro-organisms. At 70° C. the oxidation of fats is far more intensive than at the ordinary temperature. Pigments may behave similarly to linseed oilcake. C. Bottinger rubbed up 5 grammes of anti-fouling pigments in 10 grammes of linseed oil and left the mixture exposed to the air for 6 weeks. The oil was no longer taken up by ether, and as the table shows was greatly oxidised:—

BOTTINGER'S EXPERIMENTS ON OXIDATION OF LINSEED OIL IN PRESENCE OF A PIGMENT.

	Original Oil.	Extracted Oil.
d 15	0·934	0·995
Acid number . . .	13·0	25·0
Saponification number .	191·1	196·4
Iodine number . .	183·0	127

J. G. McIntosh taught in his classes for many years that he found that the residue from the extraction of linseed oil paint never ceded all its linseed oil or the derivatives of the latter to ether, and ascribed this to the formation of insoluble lead soap from the free fatty acids. The solution of the residue from ether on extraction in acids always gives an oleaginous residue which floats on the solution as oily flakes. Davis and Klein rediscovered the above fact, that porous materials expose the oil to the air over a larger surface, e.g. textiles. Fahrion used chamois leather which he soaked with linseed oil and left to dry for a week in the air. Autoxidation set in rapidly, which naturally was accelerated by increase of temperature. The oxidised oil was taken up with cold ether and was left on evaporation of the latter as a yellow more or less tacky syrup only partially soluble in petroleum ether. It yielded on analysis:—

FAHRION'S EXPERIMENTS ON OXIDATION OF LINSEED SPREAD OVER CHAMOIS LEATHER.

	Linseed Oil.	Oxidised Oil.
Iodine	175·8	66·1
Acid number	2·9	18·5
Fatty acids, per cent.	—	48·2
Oxyacids, per cent.	—	31·1
Iodine number of fatty acids . . .	—	102·8
,, ,, ,, oxyacids . . .	—	47·5

On the other hand, a test was made on a sample of linseed oil exposed to the air in a flat-bottomed porcelain basin for one year. It was not quite solid and was still a little tacky but was almost insoluble in petroleum ether and alcohol. Besides it was not completely saponifiable and gave on analysis :—

FAHRION'S EXPERIMENT ON LINSEED OIL EXPOSED FOR ONE YEAR TO AIR IN PORCELAIN BASIN.

Fatty acids, soluble in petroleum ether	42·2 per cent.
Iodine number of same	37·5 ,,
Oxyacids soluble in ether	11·4 ,,
Iodine number of same	38·0 ,,
Oxyacids soluble in alcohol	13·8 ,,
Iodine number of same	39·8 ,,

Spontaneous Combustion.—Fahrion concluded that the oxidation was accomplished by polymerisation and the formation of anhydrides. Hertkorn asserts that polymerisation accompanies oxidation. He states that oxidation first produces an acid reacting oil, prevented by the addition of alkalies or alkaline earths, whilst polymerisation is favoured. Rapid oxidation is important. In the first stage volatile apparently aldehydic bodies are formed during the whole oxidation process. In another phase acid-bodies are formed, e.g. acid anhydrides, which facilitate polymerisation. In the final stage ozone is produced, which forms nitrous acid with the air. Finally peroxides are built in the last stage of the process, but in the absence of metallic soaps solid oil containing peroxides is spontaneously inflammable. It is known that when linseed oil is blown for a long time and heated to 150 to 260° C. it separates, especially from impure oil, polymerisation products in the form of flakes and oil skins which are judiciously removed as they are liable to cause explosions. Fox ("Oil and Colourman's Journal," now "Oil and Colour Trades Journal," 1887, 8, 549) was the first to examine a blown oil. The density rose from 0·9354 to 0·986 the free fatty acids from 2·40 to 2·73 per cent. whilst the Hehner number fell from 95·7 to 87·7.

Leeds, instead of injecting air into hot linseed oil, injected oxygen and so produced two products which gave the following figures :—

	I.	II.	III.
Density	1·03	1·05	—
Free fatty acid, per cent.	18 to 28·4	18·5 to 28·9	12·67
Saponification number	221	223·5	171·6
Unsaponifiable, per cent.	0·89	0·97	0·81
Oxyacids, per cent.	42·8	44·2	31·58
Iodine number	58·8	53·5	93·9

I. Weak, II. strong, III. dried oil.

The free fatty acids could not be estimated accurately as the red coloration persisted more and more with the higher numbers for two to three minutes. Leeds examined the mixed fatty acids from the above oxidation products with the following results :—

	I.	II.	III.
Melting-point . . .	28°	27°	26°
Solidification-point . .	26°	25°	22°
Mean molecular weight .	241·4	242·5	268·8
Saponification number . .	232·4	231·3	208·7
Iodine number . . .	63·2	60·6	100·3

The molecular weight was calculated from the saponification number and doubtless is a little low, whilst the increase of the saponification number is chiefly due to the slightly acid group of oxyacids.

ULTIMATE ANALYSIS OF A SERIES OF SOLIDIFIED BLOWN OIL.

	Per Cent. C.	Per Cent. H.	Per Cent. O.	C : H.
Raw linseed oil I. .	75·03	10·78	14·19	7·0 : 1
" " " II. .	75·40	10·64	13·96	7·1 : 1
Solid linseed oil I. .	74·32	10·04	15·64	7·4 : 1
" " " II. .	69·74	9·57	20·69	7·3 : 1
" " " III. .	69·52	9·49	20·99	7·3 : 1
" " " IV. .	64·74	9·01	26·25	7·2 : 1
" " " V. .	65·40	9·00	25·60	7·3 : 1
" " " VI. .	68·64	9·24	22·12	7·4 : 1
" " " VII. .	64·38	9·01	26·61	7·2 : 1

In the above table are given the combustion results, elementary organic analysis of a series of solidified blown oils, also the combustion figures for two raw oils. Fahrion calculated the ratio of C to H in each instance, and points out that when not considerable it is at the expense of the carbon atoms. It will, moreover, be perceived that the primary reaction consists in the fixation of oxygen by the double bonds, and water is split off as a secondary reaction, as stated long ago by Mulder.

Weger has shown that in blowing linseed oil the refraction rises, also that a parallel between the refraction and the iodine number is impossible with partially oxidised oils. Long exposure has the same effect.

Under favourable conditions the autoxidation of linseed oil, diffused through a porous body, may proceed so rapidly as to cause spontaneous combustion. Fruitful but sad experience has enabled us to collect data on the absorption of oxygen by conflagrations in factories where oil is used in the dressing of woollen fabrics. According to L. Haepke cotton-wool is more inflammable than sheep's wool, as owing to its structure it can retain more oxygen, and according to Kissling silk is the most inflammable of all.

Method for Producing Spontaneous Combustion.—The open fibrous structure subdivides the oil, and is aided by the absence ol any tendency to cooling from the outside or to spread the heat. When such conditions are fulfilled then the reaction continues, until it ends in spontaneous combustion or ignition. Kissling soaked 50 grammes of cotton-wool with 100 grammes of linseed oil and pressed the mixture in a glass vessel with a thermometer in centre. This glass vessel was suspended in a second wider glass vessel protected from cold by a wooden lid. The temperature rose in 15 minutes to a maximum of 170° C. (338° F.). Spontaneous combustion did not occur until artificial heat was applied. A handful of cotton-wool was well steeped in linseed oil, well pressed in the cold, and packed with another handful of cotton-wool in a tin box. A thermometer was stuck in the middle and the whole heated in a water-bath to 99° C. In 2 hours the temperature rose to 180° C., in 4 hours great smoke appeared, and when the cotton-wool no longer smouldered it burst into flame. Schimanski and Mikoni experimented with pure wadding, which at about 180°C. (356° F.) was charred. With 1·5 per cent. linseed oil and 5 hours' heating at 90° C., it heated itself to over 150° C. (302° F.), and on 3 hours' heating at 97° C., was completely charred. Higher oil content and greater acess of air facilitated the charring. If woollen balls come in contact with oil, the latter only spreads itself on the surface of the fibre. There is enough air in the inner half of the balls to start the oxidation but not sufficient oxygen to oxidise the whole of the oil. Then the oil begins to take chemically combined water from the wool with consequent charring. Hence the increase of temperature, and when the ball is opened it bursts into flame. Erdmann and Sebzenberg soaked cotton-wool with linseed oil and led a 2 per cent. ozone stream over it. In a short time it burst into flame. Instead of subdividing linseed oil into small particles by means of textile fibres, the action of the air may be accelerated by blowing air through the oil. At ordinary temperatures no great acceleration occurs. But at higher temperatures, rapid thickening of the oil follows the absorption of oxygen. Oil blowing was discovered long before Mulder's time.

Linoleum Manufacture.—Walton, an Englishman, in 1860 described how linseed oil blown at temperatures up to 100° C. absorbed oxygen (British Patent 200 of 27/1/1860). This document describes not only the first stage of the oxidation, but how the oxidation is finished —on the principle of the thin film by passing it through a sieve and then again treating it with warm air. Rubber-like products were got in this way from linseed oil which were mixed warm with cork dust, and gum, kauri. The mixture was spread on cloth and pressed in hot rolls (British Patents 1037 of 25/4/1863 and 3216 of 19/12/1863). In this way was linoleum introduced into the industrial world.

A rival to Walton appeared later on in Parnacott (British Patent 2057, 4/9/1871). Instead of ordinary air Parnacott used compressed air. He sold the process to Taylor. Of these names only that of Walton survived. I. Hertkorn (D.R.P. 99, 710; 100, 917; 109, 583) combined the principle of fine division of the oil with strong blowing. His process depends on the principle that oxidation is much more rapid when the oil, with or without driers, is mixed with bulky imponderable matters through which hot air passes; such substances are (*a*) a mixture of cork dust, with (*b*) sawdust. The oxidation is finished in 1 to 2 hours, whereas by the above process it lasted days if not months. It is claimed that the highly elastic linoleum so made is odourless, absolutely homogeneous, and above all completely oxidised. Certain resins, e.g. kauri, are added in fine powder or dust to the partially oxidised mass. Oxides or rosinates of the alkaline earths, lime magnesia, are incorporated with the linoleum mixture to lessen the risk of the oil-saturated mass, and it is claimed that these additions impart greater hardness whilst securing a leather-like pliability not hitherto attained.

Thickening of Linseed Oil by Oxidation.—Whatever process we may adopt in the boiling of oil, the consistency or body of the resultant product is but little different from that of raw oil. Now, in many cases it is very advantageous to use an oil of good body, so as to hasten the drying when it is used either directly, or after it has been incorporated with varnish, or when it is desired to apply the oil to porous surfaces, wood, etc., without having reason to fear its being imbibed. The simplest process consists in causing the oil to fall in a thin layer, in contact with air, as we have seen in the cold process of making drying oils, but the process is a long one, and oxidation becomes difficult as soon as the oil attains a certain thickness, even when working at a temperature of 50° to 60° C. (122° to 140° F.), by which the oil is kept fluid for a longer time. Further, a quantity of oil adheres to the plates, and there solidifies, causing a serious loss when it is not desired to convert the whole into a solid body. Finally, after a time a solid pellicle is formed on the surface of the oil, which prevents oxidation, and consequently the thickening from proceeding through the mass of oil.

Attempts have been made to increase the fluidity of the oil artificially by dilution with a suitable solvent. By taking, e.g. equal parts of manganese-boiled oil and benzine, and stirring the mixture in a closed vessel, with simultaneous injection of air, rapid absorption of oxygen takes place. This absorption is stimulated by aid of heat regulated between 40° and 50° C. (104° to 122° F.). If the air be continuously injected so as to supply the quantity of oxygen necessary for complete oxidation of the oil, a quantity which amounts at least to 16 per cent. by weight of the oil used, the mixture soon thickens, and if finally we distil off the solvent a viscous residue is left on cooling. If the process be carried on so as to completely oxidise the oil, the liquid becomes cloudy owing to the formation of linoxin, which is insoluble in benzine; on separating the latter the linoxin is obtained as a very dry, elastic solid. In actual practice boiling is continued for a long time, often for 3 or 4 days, and the temperature pushed as far as 250° to 300° C. (482° to 572° F.). By this means heavy boiled oils are produced, which can be thinned down by the addition of thinner bodied oil, boiled only from 6 to 8 hours at 200° C. (392° F.). But boiling at so high a temperature has the disadvantage of liberating fatty acids, which take longer to oxidise, and render the oil fatty. In Germany preference is given to boiling oil by superheated steam or superheated air either in pans as flat as possible, so that the surrounding air may have free access, or in deep, closed pans, into which either cold or hot air is injected. In certain manufactories, especially in Holland, no drier is used; it is considered preferable to oxidise the oil exclusively by the injection of hot or cold air. The product is superior, but the process rather slow. Lewiak has taken out a patent for the injection of hot air in the production of linoleum, No. 14518, 1903.

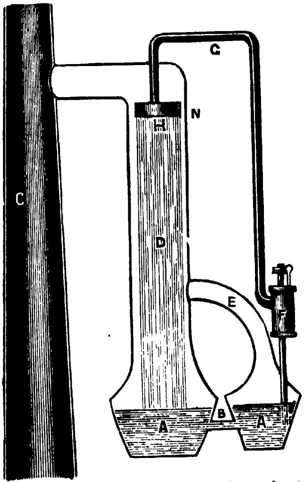

Fig. 73.—Linseed oil oxidation plant. A A, vessels containing oil communicating through B; H, reservoir with perforated bottom; N, pipe with upward current of air; D, downward shower of oil; C, chimney-stalk; E, air pressure equaliser; F, pump.

Storage of High-class Boiled Oil. — According to Livache, when a choice boiled or thickened oil is manufactured, it should not be stored either in iron or copper vessels, without electroplating the interior with silver; this deposit need not be thick, as it is subject to no wear and tear, and owing to the low price of silver would not be so costly as would at first sight appear. The same result may be arrived at, viz. prevention of discoloration by a layer of enamel which stands well and is economical. Wrought-iron vessels "galvanised" on the inside surface with tea lead which contains tin have no action on boiled oil, varnish, nor on spirits of turpentine. One per cent. of tin added to lead has the same effect.

Walton's Processes.—In F. Walton's, Lion's, Hadfield's and other processes, air acts upon oil falling in drops, so as to present a large surface to oxidation. The *modus operandi* of such processes will be understood from Fig. 74. Walton's plant is composed of a reservoir, the bottom of which, pierced with a number of holes, rests upon a second rectangular reservoir, of which two of the faces are made of glass so that the action of sunlight may intervene with the view of stimulating oxidation and bleaching the oil; the other two faces are made of perforated sheet zinc; through one of these faces air enters the whole way up the column, and passes out through the other, but owing to the minuteness of the holes and to their conical shape the oil is retained. This quadrangular column is itself surrounded by a double envelope made either totally of glass, or having two faces at least of that material, and in which an arrangement of partitions causes a current of air to flow against one of the perforated zinc faces and to force its way through the opposite. This current should not be too strong, but yet strong enough to constantly renew the air in contact with the oil. The oil at last falls into a steam-jacketed reservoir, A, by means of which it can be heated to a temperature between 100° and 170° C. (212° to 338° F.). Finally, by means of a pump similar to Fig. 74, F, the oil thus heated is propelled into the reservoir at the top of the column, through the openings of which it again passes to be submitted afresh to the action of the air. An automatic arrangement enables the flow of oil to be stopped should the pressure inside the column become too strong. Raw oil, to which an appropriate drier has been added at the start, is that which is generally treated with this apparatus. Sugar of lead to the extent of 5 to 10 per cent. is the most suitable drier. Manganese or litharge boiled oil may also be treated, but air is propelled in this case at a lower temperature, say, 100° C. (212° F.); nevertheless, in spite of this precaution, the resultant oil is darker than when raw oil is used. Another arrangement by Walton consists in boiling the oil in large open pans; the hot oil is led into a chamber maintained at a suitable temperature by steam pipes. Here the oil which falls on the floor of the chamber is beaten with armed agitators, bringing it into the form of a spray which meets a current of air passing in the opposite direction; the oil falls back again into the chamber, which may be covered with glass, so that the action of sunlight may intervene.

Storer's Process.—Instead of *blowing* air into the oil, Dr. John Storer draws it in from the atmosphere by suction by the creation of a vortex current generated by a sort of ship's propeller acting as an agitator. By a mechanical arrangement the oil subjected to the vortex action flows into another compartment and returns to the surface to expel the vitiated air, and to be again and again subjected to the same treatment. The propeller agitator makes about 1500 revolutions a minute. It will readily be seen that by the commingling of continually renewed fresh air, drier and oil are affected in a most complete and perfect manner by this process, the propelling agitator of which is horizontal. The plant differs from Vincent's in the fact that the fumes are carried away, not by a dome riveted to the pan and forming part of it, but by a hood suspended over the pan, thus allowing fresh air to be continually brought in contact with the oil without the necessity of pumping. The atmosphere above the pan is therefore always free from decomposition products. Besides Storer's agitator was horizontal and Vincent's vertical.

Solidification of Boiled Oil—Linoleum Manufacture.—When boiled oil is *completely* oxidised it is insoluble not only in ordinary boiled oil itself, but also in the whole of the various solvents used as thinners, consequently manufacturers generally are content with a partially oxidised product which will dissolve therein.

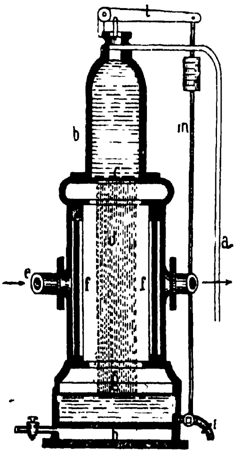

FIG. 74.

But nowadays there is a demand for completely oxidised and consequently solid oils which are incorporated by mixing and grinding with a great number of substances, to which they impart elasticity as well as insolubility in the various oil solvents as well as in acids, as in the case of linoleum manufacture. The process most generally adopted consists in spreading boiled oil in a very thin film, or oil thickened after one of the processes described, so that it may be completely oxidised; if the film be too thick surface skin is formed, when oxidation verges completion, which stops all further oxidation going on underneath, and complete solidification is prevented. When large quantities of solidified oil are required, it is necessary to have enormous surfaces at disposal, so that the film of oil to be oxidised is as thin as practicable. Two methods are in vogue: (1) Linen cloths are passed through a bath of the oil to be oxidised and so become impregnated with the oil, and are then suspended vertically, so that the excess of oil drops off. When the film of oil is dry the linen is again passed through the bath once more, and thus becomes charged afresh with oil and again exposed vertically to the action of the air, and so on until a succession of solidified layers gives the desired thickness. (2) The following is a more simple arrangement. Oil is made to fall on several thousand square yards of linen suspended vertically. The thin layer of oil absorbs the oxygen required to solidify it very rapidly. This absorption is facilitated by working in warm chambers. The sequence of operations which follow each other, almost automatically, produces very cheaply a superposition of pellicles amalgamated together to form a mass of considerable thickness. To separate the solid oil from the linen, the latter is passed between two rolls heated by steam, and so adjusted that only the linen passes through. In starting, all that has to be done is to free the linen from solidified oil for about an inch, and feed it in between the rolls; these catch hold of the linen and draw it forward, leaving the solid oil behind. But when complex substances are to be made from the solid oil, manufacturers do not trouble to separate the two, the more so as the linen does not last long. Livache tried to use oxidised oil by itself. When triturated with the majority of solvents, it swells, becomes transparent, and then divides into pieces of extreme tenuity, and so forms a paste which may be spread out in a more or less thick film. When the solvent has evaporated an elastic homogeneous surface of oxidised oil is obtained, perfectly dry and of appreciable thickness. These oxidised oil pastes may be mixed with rubber pastes or with solutions of rubber and other substances soluble in the solvents used, so as to obtain after evaporation a homogeneous product of peculiar properties partaking of those of the different substances entering into its composition.

The oil treated in the manner described until the maximum amount of oxygen has been absorbed, forms a gelatinous mass denser than water, which can be drawn into strings. It is insoluble in alcohol, ether, spirits of turpentine, chloroform and carbon disulphide. When mixed with cork dust and rosin, "fillers," etc., it is rolled into linoleum. The highly complicated machinery for inlaid linoleum, etc., is beyond the scope of this work. The following elementary analyses are by Rowland Williams:—

ELEMENTARY ANALYSES OF OXIDISED OILS FOR LINOLEUM MANUFACTURE. (ROWLAND WILLIAMS.)

	Raw Linseed.		Oxidised Linseed Oil for Linoleum Manufacture.						
	1	2	3	4	5	6	7	8	9
	%	%	%	%	%	%	%	%	%
Carbon .	75·03	75·40	74·32	69·74	69·52	64·74	65·40	68·64	64·38
Hydrogen .	10·78	10·64	10·04	9·57	9·49	9·01	9·00	9·24	9·01
Oxygen .	14·19	13·96	15·64	20·69	20·99	26·25	25·60	22·12	26·61
Ratio C : H	7·0 : 1	7·1 : 1	7·4 : 1	7·3 : 1	7·3 : 1	7·2 : 1	7·3 : 1	7·4 : 1	7·2 : 1

Reh's Linoleum Process.—Good clarified Russian linseed oil is boiled with nitric acid of known strength to decompose the glycerine and oxidise the oil. The oil treated in this way is pumped into a tank waggon which sprinkles it on to a cloth which is oxidised by hot air.

Herkhorn's Linoleum Patent.—In this process the alkaline earths and their soaps are added to the oil during boiling and oxidation, and a velvet lustre is thereby imparted to the mass. Rosin and rosinate of magnesia are added to the oil.

Pinette's Analyses of Linoleum.—Pinette analysed three samples of linoleum with the following results. His method of working is so obvious as to require no description.

ANALYSES OF LINOLEUM (PINETTE).

	1	2	3
Water	3·39	3·01	3·41
Linseed oil soluble in ether	11·43	10·60	19·58
,, ,, insoluble in ether (cork, oxidised oil)	77·24	73·63	54·16
Silica	2·94	3·99	4·31
Ferric oxide	1·78	1·79	8·86
Alumina	1·91	4·94	0·61
Lime	—	—	6·17
Alkalies	1·31	2·04	2·90
	100·00	100·00	100·00

The first linoleum manufactory was founded by Walton at Staines, near London. Old tanked oil is used, tanked for a sufficiently long time to deposit all matter in such circumstances. This oil is oxidised in two ways: (1) Oxidation by Walton's process. This si effected by the simple action of the air, by causing the oil to flow slowly over cloth suspended for the purpose. After 4 to 5 months the two sides of the cloth are covered by a layer of linoxin about 3 cm. thick. (2) Oxidation by Taylor's process. Oxygen is blown into the oil with the addition of oxidising agents, by which a less pure and less elastic linoxin is prepared in 12 hours. The shredded linoxin is boiled in steam-jacketed pans with kauri resin. The hard dark brown mass obtained is termed linoleum cement. Equal parts of cement, linoleum, and powdered cork are added with the mineral pigments. For bright pigments wood sawdust is used. The mixture is passed between four large hot rolls heated to 140° to 150° C., along with the jute fabric on which the composition is to be applied. The lustre is obtained by passing the coated cloth through polished cylindrical rolls, in the jacket of which is a freezing mixture. The large bands obtained, 150 yards long by 2 to 3 yards wide, are covered on the reverse side by a red paint by means of a finishing machine. The bands are cut into lengths of 25 to 30 yards, and dried flat in a stove. Continuous lengths of linoleum are so obtained.

Lewkowitsch analysed a so-called "scrim" oil, one produced by blowing, and subsequent oxidation in a thin film, so as to produce completely solidified linseed oil, which finds a use as massive linoleum (linoleum cement), and which is practically insoluble in all oil solvents. Nothing has been ascertained in regard to the analytical figures of solidified linseed oil, only as regards (1) the mixed fatty acids, (2) the oxyacids, and (3) the acids soluble in petroleum ether.

ANALYTICAL FIGURES RELATING TO SOLIDIFIED LINSEED OIL FOR USE IN LINOLEUM MANUFACTURE (SCRIM). (LEWKOWITSCH.)

	Solid Oil.	(1) Total Fatty Acids.	(2) Oxyacids.	(3) Fatty Acids free from Oxyacids.
I. Neutralisation number	—	209·63	—	179·97
II. Saponification „	287·47	248·74	—	187·58
III. II.—I.	—	39·11	—	7·61
IV. Iodine number	52·2	69·27	46·49	61·31
V. Total soluble acids	136·9	59·57	59·68	18·89
VI. Unsaponifiable	1·33	—	—	—
VII. Oxyacids	53·01	—	—	—
VIII. Hehner number	53·92	81·32	—	—
IX. Zinc acetyl number	—	55·04	104·99	31·36
X. Apparent acetyl number	—	115·01	164·67	50·25
XI. Saponification number of acetylated product	367·75	304·24	341·43	246·11
XII. Hehner number of acetylated product	—	84·4	76·38	96·05
XIII. XI.—II.	—	55·5	86·29	58·53

Linoxin has often to be determined quantitatively in dried coats of paint. Looked at in a certain light, it does not consist in the determination of the linoxin but that of the total oxidised and unoxidised, linseed oil. Oleic acid takes no part in the drying process, and the linolenic and the linoleic acids are not quantitatively oxidised as already stated. Mulder found in dried linseed oil only about 80 per cent. of ether-insoluble linoxin. Lately, Meister believes that linseed oil in the drying process is oxidised up to the minimum iodine number of 26·9. During linoleum manufacture, the oxidation, for various reasons, does not go so far as in the drying process. Ingle found that ether ceded 4·5 per cent. in form of a yellow crystalline mass. The total linoxin from the linoleum cedes a certain amount to ether, so Pinette must have lost sight of the fact that linoxin is insoluble in ether. This insolubility in fat solvents is only relative, as first pointed out by Livache. By prolonged treatment with benzol, the linoxin was broken up and partly dissolved, and behaved somewhat like rubber. The solution left, after evaporation of the benzol, a solid mass sticking to the fingers, which softens on warming. Livache found that the soluble portion acted as a cement for the insoluble part, the unoxidised oil, in dried coats of paint, first by saponification and then isolation of the fatty acids and oxyacids; the water soluble portion of the latter is but slight. In the case of linoleum, however, this is not so, as a large proportion of cork dust dissolves. Ulzer and Baderle give the saponification number of cork dust as 238·5, and Ingle by treating cork dust with alcoholic potash obtained :—

	Per Cent.
Cellulose	24·4
Ash	1·8
Acids soluble in ether	22·7
,, ,, ,, alcohol	5·9
,, ,, ,, water	34·4
Unsaponifiable soluble in ether	3·4
,, ,, ,, alcohol	7·4
	100·0

Ulzer and Baderle allowed benzol to act under pressure (for 1 hour at 150° C.) on linoxin, and obtained complete solution. They therefore prescribe the above method for the estimation of linoleum cement (linoxin + unoxidised oil + rosin) in linoleum. They found in various samples 13 to 25 per cent. According to Fritz this is too little; a marketable linoleum must contain, at least, 30 per cent. of linoleum-cement, which on its part usually consists of 82 per cent. of linseed oil, mostly oxidised, 12 per cent. of rosin, 5 per cent. of kauri, and 1 per cent. of castor oil. He believes that much information is obtained by replacing the benzol treatment by a benzol-chloroform extraction. Finally, he elaborated a method for extraction of the four substances for determination. Much of the newly-marketed linoleum-cement is, besides the Lincrusta factories, bought up by the large linoleum manufactories.

Action of Solvents on Linoleum. Determination of the Acetone Extract.—Acetone, like ether, extracts an indefinite amount of soluble matter. Ether—on extracting with ether a sample of the dried skin produced by the "scrim" process, 67·5 per cent. was extracted in 24 hours, but the extraction was still unfinished after 4½ months, when the extraction was 85·32 per cent. Alcohol, benzene, chloroform, and acetone yield similar extracts. Extraction by petroleum spirit of b.p. 35° to 50° C. (95° to 122° F.) also exhibits no end reaction but produces extracts differing from those yielded by other solvents. In actual practice, successive extraction (1) by petroleum spirit (24 hours), (2) of the petroleum spirit residue, by ether, gives useful results. The petroleum spirit extract is a pale greenish-yellow fairly mobile oil, and thickens but does not dry, that is, forms a skin on exposure. The ether extract of the petroleum spirit residue is a viscous, tacky, yellowish-brown oil, which dries on exposure to air, forming a fairly hard elastic skin. If the final insoluble residue be taken as linoxin, the variations in the proximate analysis of the skins produced by the scrim process are given in the following table:—

TABLE SHOWING THE VARIATIONS IN THE PROXIMATE ANALYSES OF THE PARTIALLY OXIDISED OIL OBTAINED BY THE SCRIM PROCESS.

	1	2	3	4	5	6	7
Linoxin, per cent. . .	49·57	47·08	43·62	48·41	49·22	57·09	42·46
Ether extract, per cent. .	31·16	26·79	27·93	29·38	25·45	25·16	32·91
Petroleum spirit extract, per cent. . . .	19·27	26·13	26·45	22·21	25·33	17·75	24·63

Oxidised linseed oil used for a rubber substitute or for grinding, as made at present, is practically insoluble, and therefore inapplicable for painting, and can take up from an economic point of view no further oxygen from the air. Mr. Samuel Banner, of Liverpool, patented an invention to obtain as great or even a still greater degree of oxidation than hitherto, and yet obtain oil perfectly soluble for painting. It consists in introducing into the oil, either before commencing the blowing or during the blowing from time to time, a solvent, preferably a hydrocarbon of the olefine, paraffin, or turpentine series, in such quantities that at the conclusion of the process there is sufficient solvent to keep the whole liquid. It will, of course, be evident that so long as the oil is fully liquid the solvent need not be added, but it must not be allowed to go too far in the direction of solidification to prevent the action of the solvent. Large numbers of these light hydrocarbon solvents are well known in the trade, and as they are all very much like each other, and of almost equal utility for this purpose, no rules can be given for choosing them beyond this, that hydrocarbons having boiling-points which indicate safety and free evaporating qualities are those most efficacious. By the above process the inventor obtains, dissolved in the solvents, oil at a very high degree of oxidation, which could not practically be dissolved in these same solvents if added thereto in the solidified and oxidised condition. In actual practice it is found most convenient to heat the drying oil to about 220° F. or thereabouts, and then blow, and when the temperature begins to rise the oil is cooled, and kept at about 150° F. In this process the addition of driers assists oxidation of the oil, just as it does in the ordinary one, and besides the usual oxide driers, borate and sulphate of manganese, or that compound known in commerce as acetate of manganese, may be used in order to assist the oxidation. A combined oil and solvent of this nature, with or without driers, is admirable for use as a menstruum for paints and for oilcloth making, etc. It is a quick drier, as the solvent has only to evaporate and the oxidised oil remains as a solid dry layer. A very cheap painting oil, with large body, is thus obtained, and it is to be borne in mind that in this invention the article is from beginning to end (and the final product likewise) in the liquid or viscid state, and no solid at all is produced during the operation.

CHAPTER XII.

THE TECHNICAL CHEMISTRY OF LINSEED OIL. MANUFACTURE OF RUBBER SUBSTITUTES.

INDIA-RUBBER SUBSTITUTES.

Definition.—Sulphur, sulphur chloride, and nitric acid are used respectively to convert oils (drying oils lend themselves most readily) into solid elastic substances used as rubber substitutes, the basis of which is most generally a drying oil, linseed oil, walnut oil, etc. (walnut oil is too dear and is only mentioned to show that the same results can be got with it as with linseed oil). But non-drying oils are also extensively used in Germany, and maize oil in America, in making chlorosulphuretted oil substitutes from sulphur chloride.

Practice and experience are required to get at the right proportions and the proper temperature. The published recipes are generally obsolete, fit to guide beginners in practical researches, but not for immediate and profitable use. It will suffice to describe the preparation of the two main kinds, (1) oxidised oil, and (2) vulcanised oil substitutes.

1. *Oxidised Oil, Black Substitutes.—Sacc's Experiments on the Action of Dilute Nitric Acid on Linseed Oil*[1] (*Caoutchouc des Huiles*).—Sacc, whilst working in 1846 on the saponification of linseed oil by caustic soda, examined the action of dilute nitric acid on that oil. When 100 parts of linseed oil and 200 parts of dilute nitric acid, diluted with four times its volume of water, are gently heated with continual stirring, the oil becomes brownish-red in colour; there is abundant disengagement of nitrous fumes, the oil thickens in 4 hours to a syrupy mass. Zonas in 1848, following up Sacc's experiments, first of all thickened the oil by heat, then having rendered it viscous, set fire to it, then, after having partially burnt it, so as to give it the consistency and body of a printing ink vehicle, he treated the resulting product with dilute nitric acid. This was the beginning of oxidised oil rubber substitutes (*caoutchouc des huiles*).

Sollier and Rattier's Attempts.—In 1854 F. Sollier, whether ignorant or not of above attempts, tried to convert linseed oil into a rubber substitute capable of replacing rubber in some of its essential applications. Rattier patented a similar product. *Present Process.*

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[1] See also the writer's translation of "India-rubber and Gutta-percha" (Scott, Greenwood & Son).

—Linseed oil is heated until brown and viscous (22 lb. requires 24 consecutive hours' heating) and then treated for a few hours with nitric acid, until it has assumed a thick plastic consistency, and, when cooled in the air, becomes solid. The product is freed from the excess of acid by kneading it in weak alkaline lye, until no longer acid. When cold it has the appearance of natural rubber; it is rather elastic, softens in hot water, and, unlike rubber, becomes plastic like gutta-percha. It is soluble in turps, carbon disulphide, and alkalies. Acids precipitate it unchanged from its alkaline solution.

If dilute nitric acid and linseed oil yield a product similar to that obtained by the action of sulphur chloride on oils, *vide infra*, yet in the latter product sulphur seems the active agent, which explains why the same substance is got from drying or non-drying oils. With nitric acid there is rapid oxidation exclusively confined to those oxidisable principles, viz. the unsaturated fatty acids only found in drying oils.

The oil is first heated so far as to render it viscous; it is then boiled for a long time with dilute nitric acid. A solid elastic, brown, non-tacky substance is obtained analogous to caoutchouc, whence its name of black artificial rubber. A similar substance is obtained with the different drying oils, but in proportion to the intensity of their drying properties. Linseed oil and walnut oil yield eight to ten times as much as poppy-seed oil.

Use of Rubber Substitutes made from Nitric Acid and Linseed Oil in Waterproofing Canvas, Imitation Leather. Its Application to Wood, Stone, and Metal.—As soon as discovered the product was utilised for waterproofing canvas, imitation leather for saddlery and carriage building, and travelling articles of a suppleness and fitness leaving nothing to be desired. If its use is less and less for some time back, it is still in vogue, and if but rarely used alone it is still sometimes added as an additional ingredient to articles made from pure rubber. As it adheres perfectly to all fabrics without altering them or penetrating them too deeply, the manufacturers of waterproof canvas often resort to it. It may also be readily applied to wood, stone, and metals, when it contracts a wonderful adherence.

Properties of Oxidised Oil Rubber Substitute.—This substance does not melt, but differs decidedly from the final product, *linoxin*, yielded by the complete oxidation of drying oils: by the fact that it cannot be saponified by a concentrated *aqueous* solution of potash. On heating therewith, an emulsion is obtained which does not separate on the addition of an acid. With *alcoholic* potash, on the contrary, complete saponification takes place, and the addition of an acid liberates a mixture of fatty acids of complex constitution. With carbon disulphide there is an emulsion; in petroleum the substance swells without dissolving; in a mixture of alcohol and ether it swells and dissolves if a large quantity of ether be added, whilst it is precipitated if alcohol be added in too great proportion; finally, it is soluble in ether and in a large excess of turps. Rubber substitute (from linseed oil and nitric acid) consists (1) of a mixture of substances present in the original oil and not sensibly changed by the nitric acid treatment, and (2) of products oxidised by the nitric acid and transformed into linoxin, the relative proportions of these substances masking the individual properties of each. This substance is used either in solution in ether or in spirits of turpentine in waterproofing fabrics, or is added directly in the solid state to india-rubber.[1]

2. *The Vulcanisation of Oils. Manufacture of Rubber Substitutes (White Substitute) by the Action of Sulphur Chloride on both Drying and Non-drying Oils.*—This process is due to Parkes, who, in 1855, patented a process for vulcanising linseed and rape oils by sulphur chloride. By mixing linseed oil with 5 per cent. of sulphur chloride, it becomes very thick, becoming plastic with 15 to 20 per cent., the solidity increasing as the percentage rises to 25 per cent. If the mixture be cooled solid sheets are obtained, on which other layers can be superimposed so as to obtain sheets thick enough for making printing rolls, boxes, knife handles, etc. If some carbonate of lime be added the carbonic acid evolved converts the mixture into a white spongy mass, which is mixed with natural rubber. Sulphur chloride has a similar action on other oils such as earth-nut or colza.

Nickles and Rochleder first investigated the action of sulphur chloride on fatty oils with the resulting production of a rubber substitute. Sulphur chloride mixed with any vegetable oil immediately converts it into a solid, which sometimes is very hard.

Parkes, to whom industry owes the process of vulcanising rubber by S_2Cl_2, patented a process for vulcanising linseed oil and rape-seed oil by S_2Cl_2 (British Patent of 22 October, 1855, No. 2359).

Roussin's Researches.—In 1858 Roussin described the action of sulphur chloride on oil (29 November). If we take 100 parts of linseed oil and about 25 parts of sulphur chloride a compound is obtained possessing the maximum hardness, but 100 parts of linseed oil and 15 to 20 parts of chloride yield a more supple product; and, finally, 100 parts of oil and 5 of chloride thicken the oil, it is true, but do not harden it. This latter mixture is soluble in all ordinary oils, which is not so with thicker mixtures, which only swell in these vehicles. When linseed oil is diluted with 30 to 40 times its weight of carbon disulphide, if one-fourth of the weight of oil be replaced by the same quantity of sulphur chloride, a product is obtained which remains liquid for a few days. If this solution be applied on glass, wood, etc., the carbon disulphide evaporates immediately, and a coat of varnish is soon left. Several precautions are taken so

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[1] *Synthesis of Genuine Rubber.*—The attempts that have been made to convert spirits of turpentine into real rubber have not as yet been carried out in practice.

—Linseed oil is heated until brown and viscous (22 lb. requires 24 consecutive hours' heating) and then treated for a few hours with nitric acid, until it has assumed a thick plastic consistency, and, when cooled in the air, becomes solid. The product is freed from the excess of acid by kneading it in weak alkaline lye, until no longer acid. When cold it has the appearance of natural rubber; it is rather elastic, softens in hot water, and, unlike rubber, becomes plastic like gutta-percha. It is soluble in turps, carbon disulphide, and alkalies. Acids precipitate it unchanged from its alkaline solution.

If dilute nitric acid and linseed oil yield a product similar to that obtained by the action of sulphur chloride on oils, *vide infra*, yet in the latter product sulphur seems the active agent, which explains why the same substance is got from drying or non-drying oils. With nitric acid there is rapid oxidation exclusively confined to those oxidisable principles, viz. the unsaturated fatty acids only found in drying oils.

The oil is first heated so far as to render it viscous; it is then boiled for a long time with dilute nitric acid. A solid elastic, brown, non-tacky substance is obtained analogous to caoutchouc, whence its name of black artificial rubber. A similar substance is obtained with the different drying oils, but in proportion to the intensity of their drying properties. Linseed oil and walnut oil yield eight to ten times as much as poppy-seed oil.

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Rubber Substitute from Maize Oil.—The manufacture of rubber substitutes is so simple as to lie easily within the means of ordinary factories. It is assumed that the factory has ordinary conveniences, and gas is laid on, as in the manufacture of "black sub"; great heat is supplied by gas quickly and economically. A cylindrical tank or boiler should be provided holding one or more barrels of corn oil, and placed so that it may be filled at its top. Such a tank, in the factory basement, could be filled from barrels on the main floor with little trouble or waste by placing the tank immediately beneath the floor, which is provided with a small hatchway or trap-door. The tank should be filled with faucet for drawing off oil as required, or oil may be piped directly to the boiling-kettle. Gas jets are arranged around the base of this tank, so that its contents can be heated in advance, an economy in time. Within easy distance of the tank should be another cluster or circle of gas jets in a chamber shut in at the sides, open at the top, properly constructed, and of a strength to sustain an 8-gallon pan. Still another cluster of gas jets should be provided over which sulphur can be melted. Also a cooling box, 2 by 3 by 5 feet, constructed of wood. The apparatus now consists of an iron boiler for holding the supply of corn oil, a heater for boiling the oil, a heater for melting sulphur, and a cooling box. Two strong men are required to handle the work properly. Eight gallons of corn oil are drawn off from the tank, and 20¼ lb. of sulphur weighed into a large dipper, and each placed over its respective heater. The oil, having been previously heated, attains the boiling-point quickly, and for 30 minutes should be kept at a temperature of 470° F. and constantly stirred. The sulphur, being now melted, is added to the boiling corn oil. It must be added hot to prevent crystallisation. The workmen must be prepared for prompt and skilful action at this point, for no sooner does the sulphur mix with the boiling oil than the contents of the kettle rise rapidly, and before it can boil over must be removed and emptied into the cooling box, where it is stirred. When cold it is dumped upon and tied up in large cloths, or placed in pans ready for use, as convenience or necessity suggests. In this manner black substitute is manufactured. The boiling will reduce the quantity somewhat, say 2 per cent., and from a weight of 69¼ lb. of material a batch should result weighing about 68 lb. It will be noted that something over 41 per cent. of sulphur is required to make this substitute, while to oxidise (vulcanise) cotton-seed oil or rape-seed oil requires but 26 per cent. A recipe which has been given for making sulphur chloride substitute from rape-seed oil is as follows:—

Rape-seed oil	½ gallon.
Benzine	1 „
Sulphur chloride	14 ounces.
Magnesia	½ „

The above-described rubber substitutes are sometimes employed in waterproofing cloth, water pipes, etc.; sometimes in combination with natural supple rubber for other industrial uses.

Only one class of organic compounds plays an important rôle in the rubber industry, viz. the products sold as rubber substitutes, artificial rubber or imitation rubber, made by heating oils, whether drying or non-drying, with sulphur or sulphur chloride, and the non-sulphuretted substitutes made by oxidising linseed oil.

Waterproof Varnish from Vulcanised Oil (Fr. Pat. 480,038, M. Poto).—Oils vulcanised with sulphur chloride are dissolved in amyl acetate, the following typical method of preparation being followed: One thousand parts of castor oil are mixed with 2000 of amyl acetate, and stirred up well with 250 parts of sulphur chloride. In a short time the mixture sets to a fairly solid jelly, and gives off large quantities of hydrochloric acid vapour from the acetyl chloride formed during the reaction. If, however, the product be left in a tightly closed vessel for several days it will be found to have become completely liquefied and dissolved. The acid reaction is neutralised, preferably with barium carbonate, and after the precipitate has been removed by decantation and filtering, a clear, almost colourless, liquid is left, consisting of a perfect solution of the vulcanised oil, hitherto regarded as insoluble. This solution may be employed, as it is, for waterproofing fabrics, leather, paper, etc. On the other hand, if it be mixed with other solvents, such as alcohol, benzol, acetone, acetic ether, etc., and employed to dissolve a certain proportion of nitrocellulose, there results an excellent varnish for glossy leather—the gloss resisting the action of soap, friction, etc.—a leather polish, a varnish for oil cloth, and when mixed with pigments, a waterproof, quick-drying paint which will stand washing and changes of temperature.

Analysis.—Substitutes are generally met with in the form of yellow or brown elastic masses, without cohesion, breaking up under pressure, greasy and moist to the touch. Two of these substances gave the following results :—

TABLE SHOWING THE PARTIAL ANALYSIS OF TWO RUBBER SUBSTITUTES.

	I.	II.
Water	1·00	0·85
Sulphur	6·17	6·4
Ash	5·52	0·8

Substitutes behave towards solvents like rubber itself ; insoluble in alcohol, they only dissolve with difficulty and incompletely in benzol, carbon disulphide, turps, etc. To detect the presence of oils or fats in manufactured rubber, a method has been proposed which yields, in experienced hands, useful results. The rubber is digested in carbon disulphide to which 5 per cent. of turps has been added, the solution is filtered after a few hours, and distilled. An appreciable residue indicates the presence of foreign bodies of a fatty nature. The method has several drawbacks: first, vulcanised rubber is slightly soluble in the mixture of carbon disulphide and alcohol ; the experiment is not conclusive unless the fats are present in notable quantity ; finally, sulphur is likewise dissolved, and may give rise to error. In spite of these drawbacks, from a qualitative point of view, the method, applied with discretion, may yield useful indications. For a quantitative estimation the process cannot be adopted, because the substitutes only dissolve partially, even when isolated and repeatedly digested in alcoholised carbon disulphide. The sorts examined left after solution a residue of 20 to 30 per cent. of their weight, and on each treatment still further lost 1 to 2 per cent., so that it cannot be admitted that the substitute is insoluble, and that it is the proportion of unchanged oil or fat which alone dissolves. Substitutes dissolve completely in petroleum at a high temperature, as vulcanised rubber does itself. Ligroin only dissolves them partially. Aqueous soda dissolves them with difficulty and incompletely. The action of alcoholic soda is dealt with further on. Hübl's iodine addition method seemed likely to prove useful, for rubber hardly absorbs iodine, whilst sulphuretted oils should readily fix iodine, like the oxidised oils which almost retain their primitive iodine value. Preliminary experiment led to this unexpected result: *sulphuretted oils do not absorb iodine and behave like quasi-saturated compounds.* Henriques tried to separate the sulphur from the substitutes and to isolate and weigh the regenerated fatty acids. He treated the substitutes with alcoholic soda, to which different salts that absorb sulphur were added—salts of lead, mercury, copper and zinc; but in whatever way treated, the fatty acids, isolated from the alcoholic lye, varied in quantity, and always contained equally variable quantities of sulphur. He tried, without success, to effect saponification and desulphurisation in a closed vessel at a high temperature, by replacing ethylic alcohol by amylic alcohol. However, substitutes dissolve freely and completely in alcoholic soda, and on this fact is based an approximate method of analysis. Sharp and complete separations as in inorganic analysis are here quite impracticable. Results are only approximate. We have to deal with very complex mixtures, like rubber itself, which may contain substances belonging to different classes of bodies. The following experiment shows that substitutes, or at least their organic constituents, are completely soluble in alcoholic soda: 1 gramme of substitute was boiled in a flask attached to a reflux condenser, with an excess of caustic soda (7 to 8 per cent. Na_2O). After a few hours the alcohol was distilled off, the residue dissolved in water, and filtered through a tared filter.

Weight of the dry residue	0·041 = 4·1 per cent.
,, ,, ,, ash	0·0413

The residue, therefore, contained no trace of organic matter. Another substitute which left no ash dissolved completely. Both white and brown substitutes are slightly yellowish, clotted, elastic masses, with a neutral reaction and a slightly penetrating oleaginous odour. Water extracts nothing; acids and alkalies but little; neither do the majority of neutral organic solvents. The characteristic of these products is their high chlorine content—almost as high as their sulphur content. From their behaviour with solvents the chlorine should exist in organic combination. If the substitutes examined result from the action of chloride of sulphur upon oils, that reagent has entered entirely (chlorine and sulphur), into the molecule of the proximate constituents of the oil. In order to facilitate the explanation of the results, Henriques' analyses are given on the next page.

TABLE SHOWING ANALYSES OF COMMERCIAL RUBBER SUBSTITUTES.

	White Substitutes.			Brown Substitutes.	
	A	B.	C.	A.	B.
Sulphur in the substitute	6·4	6·17	8·25	15·48	17·71
Chlorine ,, ,,	5·0	5·86	8·88	0·7	0·36
Water ,, ,,	0·85	1·0	—	—	—
Ash in the substitute	0·8	5·51	—	—	—
Percentage of fatty acids	90·45	73·58	—	—	—
Sulphur in the ,, ,,	6·12	6·45	8·15	14·14	15·20
Chlorine ,, ,, ,,	0·83	0·43	—	—	—
Iodine value of the substitute	30·9	31·0	32·6	42·0	42·0
,, ,, ,, fatty acids	91·3	91·2	102·3	129·0	125·6

The determination of the sulphur of substitutes involves the same precautions as rubber. Oxidation by nitric acid, followed by fusion with an alkaline oxidising agent, alone yields concordant results. To estimate the chlorine, nitrate of silver was added to the nitric acid, so as to avoid all loss by volatilisation of the hydrochloric acid. After alkaline fusion, the whole is digested in water, the insoluble silver compounds are separated (generally metallic silver), and the sulphur is estimated in one portion of the liquid as barium sulphate, and the chlorine by titration with nitrate of silver and sulphocyanate. As already mentioned, oils solidified by sulphur chloride absorb only insignificant quantities of iodine. Sample A in the table, for example, gave an iodine number of 7·2 (Hübl), and this number is only apparent. The feeble iodine absorption is partly due to the product being almost insoluble in chloroform. By frequently agitating the finely divided substitute in suspension in that liquid with excess of iodine solution, and leaving it in contact for twelve hours, Henriques obtained from sorts A and B, table, iodine values of 30·9 and 31. Compared with the iodine values of the drying oils used to make these substitutes, these figures are very low. Sulphur chloride seems partially to saturate the free valencies of the oil as much by its chlorine as by its sulphur, possibly by its chlorine alone. Substitutes treated with iodine, in chloroformic solution, strongly retain the metalloid, and it is necessary in the back titration by thiosulphate to stir energetically and for a long time so as to destroy all iodine in excess.

Substitutes are completely soluble in alcoholic soda, *vide supra*. In this reaction, the chlorine is almost eliminated, whilst the percentage of sulphur in the fatty acids corresponds exactly with the percentage of sulphur in the substitute. However, the proportion of fatty acids found is always lower than simple saponification would imply, even taking into account the elimination of the chlorine. Thus, Sample A gave 90 per cent., Sample B only 74 per cent. of fatty acids. A portion of the oil and a corresponding quantity of sulphur must thus have undergone a different transformation. The liquid from the saponification contains much chlorine but no apparent sulphur nor sulphuric acid, sulphuretted hydrogen nor sulphurous acid. But on evaporating these liquids in presence of the excess of hydrochloric acid added to liberate the fatty acids to the point where hydrochloric acid fumes begin to be given off, the presence of much sulphuric acid is demonstrated. It would seem, therefore, that the sulphur chloride with the assistance of oxygen borrowed either from the air or the substitute itself, transforms a portion of the oil into a sulpho-oleic acid analogous to those produced in the manufacture of turkey-red oil. In all substitutes made by Henriques these sulpho-oleic acids were formed, in greater or less quantity, with a consequent diminution of substituted fatty acids. These concomitant reactions are difficult to regulate, for even when working under apparently identical conditions, he obtained variable proportions of insoluble fatty acids. As saponification eliminates chlorine from the molecule of the substitute, it was to be foreseen that the isolated acids would appreciably absorb more iodine than the substitutes from which they were derived, whilst the ordinary fatty acids yield, as is known, an iodine value approaching that of the oils from which they were derived. In fact, *the iodine values of the fatty acids are almost triple those of the substitutes.* Little is known of the action of sulphur chloride (S_2Cl_2) on fatty oils. Warren asserts that drying oils yield solid masses with sulphur chloride *insoluble* in carbon disulphide, whilst the non-drying oils yield products *soluble* in that solvent.

Stolmann, in the last (German) edition of Muspratt's "Dictionary," writes that these results are unreliable, as olive oil—the type of the non-drying oils—is transformed by sulphur chloride into a rubber-like mass, insoluble in ether. Sommer's patent specification as well as Henriques' results, formally contradict Warren's assertions. If a sufficient quantity of sulphur chloride be added to a fatty oil, the two liquids soon mix. Energetic reaction soon sets in, with great evolution of heat. The mixture froths, rises, gives off vapours of sulphur chloride, with a little hydrochloric acid and sulphurous acid gas; after a few seconds the whole becomes converted into a solid, elastic, scarcely tacky mass that can be ground and crushed under the pestle. Exposed to the air, the mass loses the excess of sulphur chloride used and the adherent hydrochloric acid; it then resembles in every way commercial white rubber substitutes. If one or other of the reagents, or both, be diluted with a neutral solvent, carbon disulphide or benzol, the reaction is longer in being manifested, its violence is moderated, but the final result is the same. The substitute is a little more porous in consequence of the volatilisation of the solvent. That is how the reaction goes on in presence of a sufficient quantity of sulphur chloride. In the contrary case, along with a less disengagement of heat, a pasty, tacky residue is obtained, which even a long time afterwards, whether in the hot or in the cold, does not solidify. The quantity of sulphur chloride required to convert an oil into a solid substitute varies with the nature of the oil, according to Henriques' experiments thus:—

TABLE SHOWING THE NUMBER OF LB. OF SULPHUR CHLORIDE REQUIRED TO CONVERT 100 LB. OF DIFFERENT VEGETABLE OILS INTO WHITE INDIA-RUBBER SUBSTITUTE. (HENRIQUES.)

100 parts of oil of	do not yield a solid product with Parts S_2Cl_2.	but do so well with Parts S_2Cl_2.
Linseed	25	30
Poppy	30	35
Rape	20	25
Cotton	40	45
Olive	20	25
Castor	18	20

These figures show that there is no relation between the drying properties of oils and their aptitude to solidify under the action of sulphur chloride. Having fixed the proportions of sulphur chloride, Henriques prepared and analysed substitutes with linseed oil, rape oil, and poppy oil bases, and with a mixture of equal parts of linseed oil and rape oil.

TABLE SHOWING ANALYSES OF SPECIALLY PREPARED SUBSTITUTES.

	A.	B.	C.	D.	E	F.	G.	H.	I.
Sulphur in the substitute	9·34	4·78	8·28	6 59	7·68	—	4·82	10·6	6·23
Chlorine ,, ,,	8·84	4·85	7·62	5·95	7·44	—	6·70	8·95	5·36
Water ,, ,,	3·02	0·85	—	—	—	—	—	—	—
Ash in the substitute .	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0
Percentage of fatty acids	79·6	1·67	86 89	87 95	74·90	—	85·35	—	—
Sulphur in these acids .	9·88	4·06	8·34	6·54	8·32	—	5·32	—	6·44
Chlorine ,, ,,	Traces.	0·60	Little.	Little.	—	—	0·26	Traces.	Traces.
Iodine value of the substitute . . .	56·3	52·6	32·5	29·9	33·6	42·8	35·2	21·9	30·3
Iodine value of the acids	160·3	141·2[1]	101·5	102·8	133·3	129·2	136·2[2]	143·5	91·5
Acetyl ,, . . .	21·0	19·6	31·0	—	—	—	—	105·6	51·3

A, Raw linseed oil (fresh). B, Oxidised oil. C, Rape oil (fresh) D, Oxidised rape oil. E, Oxidised poppy-seed oil. F, Mixture of oxidised linseed and poppy oils. G, Castor oil with a minimum dose of chloride of sulphur. H, Castor oil with a maximum dose of chloride of sulphur. I, The oil termed soluble castor (oxidised cotton-seed oil).

The results are given in the table. Neither of these substitutes are analogous with the substitutes A and B of the previous table, products of English origin, of which it would be desirable to know the method of preparation. On the contrary, the commercial sample C (previous table) yielded, on analysis, figures so similar to those of the rape oil substitutes C, of above table, that they may be rightly regarded as identical. The iodine numbers of the fatty acids isolated from substitutes show such wide differences from one kind to another that agreement in the iodine numbers may be taken as proof of identity. Moreover, Henriques *learned from a manufacturer that the bulk of the substitutes made in Germany are made from rape oil.* The distinctive character of the English substitutes A and B is their relatively low percentage of sulphur, according to which only 20 per cent. of sulphur chloride had been used to solidify the oil. With the exception of castor oil, only *oxidised* oils can be solidified with that proportion of sulphur chloride.

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[1] Another determination gave iodine value = 121·0.

[2] Two other determinations gave 147 and 152·1.

Raw linseed oil, for example, which requires at least 30 parts of sulphur chloride, S_2Cl_2, to solidify it when it is fresh, only requires 15 to 18 per cent. when it has been heated for some hours at 200° to 250° C. (say 392° to 482° F.). If the temperature be pushed to 250° to 300° C. (482° to 572° F.), 10 per cent of S_2Cl_2 suffices. A substitute prepared would run into 4·78 per cent. of sulphur and 4·85 per cent. of chlorine. All drying oils behave in this respect like linseed oil.

Henriques thus identified the English substitutes with the product obtained by the action of sulphur chloride on oxidised cottonseed oil, known in the English trade under the name of soluble castor oil, "lardine".

Brown Substitutes.—These occur as deep brown, tacky blocks, sometimes in powder. Analysis shows a greater quantity of sulphur than in the substitutes previously examined. But chlorine is almost entirely absent. They are undoubtedly obtained by heating oil with sulphur. *They also dissolve in alcoholic soda;* the soap, treated by an acid, disengages appreciable quantities of *sulphuretted hydrogen;* the isolated fatty acids, however, contain a smaller proportion of sulphur than the substitutes from which they were derived.

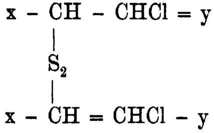
Their iodine value and those of their fatty acids is rather high; a mixture of hemp-seed, rape, and linseed oil, or a mixture of linseed and rape oil, is used in their manufacture. Henriques did not pursue the examination of these substitutes, which are much less interesting from the scientific point of view. To ascertain whether vulcanisation of rubber, sophisticated with substitutes, influenced the percentage of chlorine in the product, Henriques examined a number of manufactured rubbers containing substitutes, and always found chlorine in appreciable quantity. As no other chlorinated compounds, with one exception, are used in the manufacture of rubber, we may conclude that *the presence of chlorine in the alkaline alcoholic extract of a rubber is due to the use of a white substitute.* Quantitative tests, however, showed that the proportion of chlorine in manufactured rubbers is much less than that which corresponds with the quantity of substitute added. Thus, in two samples the percentage of substitute of which came out at 53 and 12 per cent., Henriques found only 0·5 and 0·37 of chlorine, whilst calculating on an average of

7 per cent. chlorine in the substitute, Henriques ought to have found 3·7 and 0·9 per cent. Cl. On vulcanisation, a portion of the chlorine is therefore disengaged either in the form of sulphur chloride, or as hydrochloric acid. If alcoholic soda extracts an appreciable quantity of substance from rubber, and the extract contains no chlorine, we can decide whether the rubber is mixed with brown substitute or contains a fatty body. The fatty acids liberated from substitutes contain slightly less sulphur than the substitutes themselves. Those of brown substitutes generally contain more than 10 per cent. If, therefore, the fatty oils have not absorbed sulphur during vulcanisation—if they have not by the heating itself of the rubber been converted into substitute—we should be able, by isolating the fatty acids from the treatment with alcoholic soda, and by estimating their percentage of sulphur, to distinguish between the addition of an oil heated with sulphur and an ordinary oil. In order to solve this point experimentally, Henriques heated rape oil with excess of sulphur for several hours at a temperature of 130° to 135° C. (266° to 275° F.), the highest temperature reached in vulcanisation. The oil dissolved large quantities of sulphur, which for the greater part recrystallised out on cooling. After filtration the limpid oil was saponified, and the fatty acids separated. Finally, the latter were dissolved in 90 per cent. alcohol to separate the precipitated sulphur, and the sulphur was estimated in the acids thus purified, in which were still deposited some crystals of sulphur after filtration. Found sulphur = 0·98 per cent.

The quantity of sulphur so found may be neglected when compared with that which brown substitutes contain. The problem to detect in a rubber the presence of white substitute, brown substitute, or an ordinary fatty oil, and to estimate them therein, may therefore be regarded as solved. The presence of notable proportions of chlorine points to the addition of white substitute. The estimation of the sulphur in the fatty acids liberated from the alcoholic soda extract decides between brown substitute and a fatty oil. The method is at fault if a rubber contains all these three categories of substance simultaneously, but evidently that occurs very rarely.

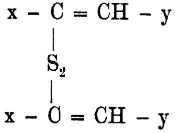
The following diagrams show the chemical constitution of white substitute (1) before, (2) after saponification:—

(1)



$$\begin{array}{l} x - CH - CHCl = y \\ \quad\;\; | \\ \quad\;\; S_2 \\ \quad\;\; | \\ x - CH = CHCl - y \end{array}$$

(2)



$$\begin{array}{l} x - C = CH - y \\ \quad\;\; | \\ \quad\;\; S_2 \\ \quad\;\; | \\ x - C = CH - y \end{array}$$

CHAPTER XIII.

TIME OF DRYING AND CHEMISTRY OF DRYING PROCESS.

Chevreul was one of the first to experiment on the rapidity of drying of linseed under varying conditions. The accompanying two tables speak for themselves:—

TABLE SHOWING TIME TAKEN BY (1) RAW LINSEED OIL, (2) LINSEED OIL AND WHITE LEAD, (3) LINSEED OIL AND WHITE ZINC TO DRY ON DIFFERENT IMPERVIOUS SURFACES. (CHEVREUL.)

	Linseed Oil.				Linseed Oil and White Lead.				Linseed Oil and White Zinc.			
	1st Coat.	2nd Coat.	3rd Coat.	Total.	1st Coat.	2nd Coat.	3rd Coat.	Total.	1st Coat.	2nd Coat.	3rd Coat.	Total.
	Days.	Days.	Days.	Days.	Days.	Days.	Days.	Days.	Days.	Days.	Days.	Days.
Glass .	3	6	4	13	3	2	2	7	4	3	3	10
Copper	5	7	5	17	2	2	2	6	2	4	4	10
Brass .	2	5	5	12	2	2	2	6	3	4	3	10
Zinc .	3	5	5	13	3	2	2	7	4	3	3	10
Iron .	3	6	4	13	3	2	2	7	3	3	3	9
Lead .	4	5	3	12	4	2	2	8	1	4	4	9

TABLE SHOWING THE RAPIDITY OF DRYING OF DIFFERENT COATS OR FILMS OF LINSEED OIL, BOTH *RAW* AND *BOILED* WITH AND WITHOUT DRIERS OF DIFFERENT KINDS AND ON DIFFERENT SURFACES: A, B, C, OAKWOOD; D, E, F, G, GLASS. (CHEVREUL.)

	A.	B.	C.	D.	E.	F.	G.
No. of Coat.	Days.	Days.	Days.	Days.	Days.	Days.	Days.
1	99	41	2	6	4	½	2
2	6	4	3	6	5	4	4
3	3	4	2	5	5	2	4
Total Days .	108	49	7	17	14	6½	10

Oakwood Surface.
A = *raw* linseed oil tested against B.
B = *raw* linseed oil boiled for 3 hours.
C = *raw* linseed oil boiled for 3 hours with $\frac{1}{10}$ per cent. of litharge, which shows that heat does not act by itself alone as the litharge-treated oil dried 7 times more rapidly.

Glass Surface.

D = *raw* linseed oil.

E = *raw* linseed oil heated not higher than 70 to 80° C. for 6 hours. It will be seen that it dries better on glass than the raw oil D.

F = *raw* linseed oil heated to 70 to 80° C. with 10 per cent. of manganese peroxide; the oil then dried in half the time it took in E.

G = *raw* linseed oil boiled with 10 per cent. manganese peroxide. The time occupied in drying was increased compared with F.

To prevent surface drying, which would stop the liquid underlayer from absorbing oxygen, Mulder urged the need for spreading the oils out thinly. He spread 3 grammes of oil over 220 square centimetres (about 0·015 gramme of oil per square centimetre). He noted the following increases:—

OXYGEN ABSORPTION, PER CENT., AND TIME TAKEN BY VARIOUS SAMPLES OF LINSEED OIL TO DRY WHEN SPREAD OUT IN LAYERS OF DIFFERENT THICKNESSES. (MULDER.)

Days.	Thickness of Film.		
	35 mg. per sq. cm Oxygen Absorption, per Cent.	3 mg. per sq. cm. Oxygen Absorption, per Cent.	3 mg. per sq. cm. Oxygen Absorption, per Cent.
1	—	1·2	—
2	—	4·3	—
3	0·05	7·3	0·2
4	—	11·1	—
5	0·1	—	—
6	—	16·6	—
7	—	16·9	—
8	—	17·1	4·9
10	0·5	—	—
13	—	16·4	—
14	—	—	17·0
15	2·9	—	—
18	—	14·1	17·7
21	—	—	—
22	—	—	18·1
24	—	12·4	—
26	—	—	18·1
29	10·5	—	—
32	—	13·2	—
36	10·7	13·6	17·7
39	—	—	—
43	10·3	—	16·3
46	—	11·2	—
50	10·2	—	15·3
58	—	11·2	—
64	—	—	15·3
71	—	—	15·3
88	10·6	—	—
91	—	10·8	—
109	—	—	15·8
112	10·6	—	—
115	—	10·0	—
255	—	—	14·7

With regard to column I. of table. Owing to the length of time occupied by the experiment no comparison can be made. Mulder took the figure 10·6 as correct, even though he found much higher numbers in similar experiments (see columns II. and III.). Mulder did not overlook that the thicknesses of the films (columns I. and II.) are completely different, so that in the plates with closely agreeing end results, 10·6 and 10·0 above given, the lower layer of the film is untouched. This is quite correct, and was due to the thickness of Mulder's films. In the case of column I., with thick layer the maximum of 10·6 per cent. was attained in 88 days, and in the case of column II., with the thinner layer, in 8 days with 17·1. This maximum meant nothing to Mulder, neither was it of any importance in a third research (column III.) which he undertook. The experiment was made on linseed oil treated with conc. H_2SO_4 (column III.). It will be seen how the oxygen absorption decreased during Mulder's protracted experiment. He believed that sulphuric acid saponification had occurred and tested the linseed oil for free fatty acids by shaking it with alcohol and precipitating the solution with lead acetate; he only got a very small precipitate. Moreover, he found no difference although the dried linseed oil was darker. He tried to explain the decreased absorption by assuming that, normally, oleic acid is volatile; here, from an absorption point of view, it formed fixed oxidation products. He therefore ascribed the increase in weight, during the drying of the linseed oil, to oxygen absorption, and the decrease in weight that followed, to the escape of volatile substances; therefore the apparent oxygen number of the oil was 11 per cent. Mulder made a similar experiment with his linoleic acid. With a film of thickness of 24 milligrammes per sq. centimetre, in 28 days he found an oxygen number of 17·9, with 29 milligrammes in 23 days he found 20. The linoleic acid by that time had, moreover, become solid, but viscous and tacky.

TABLE SHOWING OXYGEN ABSORBED PER CENT. BY WEIGHT BY LINSEED OIL WITH AND WITHOUT DRIERS. (MULDER.)

Oil Alone.	Increase in Weight, per Cent.	Oil Plus Drier.	Increase in Weight, per Cent.
Poppy-seed . . .	12·2	Linseed and manganese borate . . .	12·4
Walnut	8·7	Linseed and litharge .	12·5
Linseed . . .	11·9	„ „ red lead .	13·2

In a later experiment a so-called boiled oil was used containing 2·6 per cent. PbO. The air issuing from the flask was first passed through calcium chloride tubes, which retained (1) water, (2) formic, and (3) acetic acid, then through soda lime tubes to absorb (4) CO_2. Air was passed through the oil for 2 days with the following result:—

Increase in weight of oil	0·92 per cent.
Found H_2O, CH_2O_2, $C_2H_4O_2$	1·06 „
„ CO_2	0·18 „

Quite different results were found when the air was passed over the oil for 23 days:—

Increase in weight of oil	2·03 per cent.
Found H_2O, CH_2O_2, $C_2H_4O_2$	2·73 „
„ CO_2	0·57 „

The ratio of the absorption (increase in weight) to the loss in weight is 1 to 1·35 and 1 to 1·163. The ratio of

$$H_2O + CH_2O_2 + C_2H_4O_2 \text{ to } CO_2$$

is 5·9 to 1 and 4·8 to 1. From such wide differences as these it must be concluded that the nature and amount of the volatile substances differ under different experimental conditions.

Kissling passed a stream of dry air free from CO_2 through linseed oil at 100° C. (212° F.). The air on exit passed (1) through a vessel containing conc. H_2SO_4 then (2) through another containing caustic soda solution. The daily increase in weight throughout was

Of the oil	0·41 gramme.
„ H_2SO_4	0·39 „
„ NaHO	0·07 „

The last figure was estimated by titration and calculated as CO_2. Small amounts of formic and acetic acids were also found. Mulder's and Kissling's results show that the loss in weight is greater than the net increase in weight. Fahrion suggested the net increase in weight as the apparent oxygen number, analogue of the iodine number. It must be recognised that the net increase in weight is only apparent; this is brought about by a correction to the true oxygen number, viz. the total amount of oxygen entering into the reaction expressed as per cent. of oil. It is thus evident that the true oxygen number can only be determined gasometrically. Mulder estimated the apparent oxygen number thus: He coated tin plates of 250 sq. centimetres or 150 sq. centimetres with a film of linseed oil and left them exposed to the air. The plates were weighed from time to time. Mulder gave the increase in weight in absolute numbers. At the end of the experiment the sum of the negative numbers was deducted from the positive numbers, and the difference calculated to per cent. of original oil, the increase in weight being defined as apparent oxygen numbers. Fahrion, better to appreciate Mulder's results, calculated them to per cent. of oil.

The Oxidation and Consequent Drying of Linseed Oil on Porous Media.—There was a long lapse of time from Mulder till 1883, when

Achille Livache brought forward a new method. Chevreul had described long before how linseed oil spread on such impervious media as sheet-lead, dried quicker, also on porcelain, glass and gypsum, whilst sheet-copper, zinc, brass, iron only slightly accelerated the process. Livache replaced sheet-lead by lead in powder.

Experiments with Copper Powder to Replace Livache's Lead Powder.—Hübl recommended copper powder in place of lead powder, which he claimed gave results corresponding better with the iodine number of the oil. But Weger has shown that such a comparison between the oxygen number and the iodine number is impracticable.

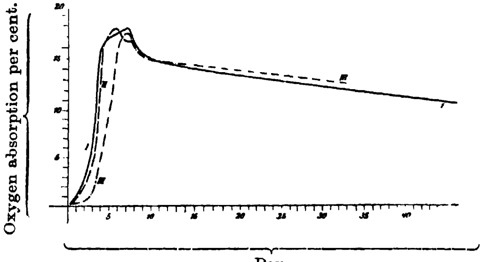


FIG. 75.

Fig. showing graphically the effect on the rapidity of drying and oxygen absorption per cent. of weather, temperature, percentage of moisture in surrounding air and oxygen content of the superincumbent atmosphere on one and the same sample of oil tested at somewhat lengthy intervals.

In any case, copper powder seems to be at least as effective as lead powder. Lippert's experiments at least prove it. The test is made thus: On a glass basin, 10 to 12 centimetres diameter, 8 to 10 grammes of commercial copper powder, sometimes covered with a slight film of cuprous oxide, and then without stirring, 60 drops 0·6 to 0·7 gramme of linseed oil was dropped on to it. If more or less be taken, other numbers will be found. However, working as above, two comparative estimations may be made, the results of which agree. The maximum increase in weight is determined on the second, third, or fourth day. The following are the results of five experiments:—

TABLE SHOWING THE RESULTS OF FIVE EXPERIMENTS ON OXYGEN ABSORPTION BY COPPER POWDER. (LIPPERT.)

Oxygen Number.	Flanders Varnish Linseed Oil.	The Same Heated rapidly to 305° C. (581° F.).	Indian Linseed Oil, Old	Dutch Varnish Oil.	Dutch Linseed Oil, Raw Fresh.
1 day . .	5·4	—	14·3	9·1	1·2
2 days . .	16·5	11·4	16·6	17·6	12·5
3 „ . .	17·8	17·4	15·7	17·4	—
4 „ . .	17·4	17·9	—	—	19·3

PERCENTAGE OF OXYGEN ABSORBED BY DIFFERENT STRIPS OF CHAMOIS EXPOSED TO THE AIR AND IMPREGNATED WITH DIFFERENT OILS AND COMPARED AGAINST A BLANK STRIP.

	Iodine Value.	Absorption of Oxygen in 100 Parts of Oil after														Maximum.	Absorption according to Livache.	Calculated from the Iodine Value 1 × 0·063.
		1 Day.	2 Days.	3 Days.	4 Days.	5 Days.	6 Days.	7 Days.	8 Days.	9 Days	10 Days.	14 Days.	21 Days.	28 Days.	56 Days.			
Blank Test .	—	0·0	1·0	1·3	0·9	1·4	– 0·6	1·3	0·0	0·5	1·8	– 0·5	1·1	3·3	– 2·5	—	—	—
Olive oil . .	82·1	0·2	1·0	1·2	0·9	1·4	– 0·4	1·1	– 0·1	0·5	1·7	– 0·5	0·7	3·5	– 2·5	0·2	1·7	5·2
Sesame oil .	110·2	0·1	1·2	0·9	0·5	1·1	– 0·5	1·0	0·0	0·7	2·0	1·1	4·7	6·6	– 0·5	3·6	2·4	7·0
Rape oil . .	102·4	0·1	1·1	1·3	1·0	1·8	0·5	2·5	2·0	2·8	4·6	2·3	3·2	6·3	– 0·2	2·8	2·9	6·5
Cotton-seed oil	109·2	– 0·1	0·8	1·4	1·2	3·1	2·2	5·0	4·7	5·7	7·4	2·5	1·6	5·2	– 1·4	5·6	5·9	6·9
Poppy-seed oil	135·9	0·3	2·0	3·2	4·3	7·1	7·3	9·7	7·0	7·3	8·0	3·3	2·7	6·7	– 0·3	8·4	6·8	8·6
Walnut oil .	149·2	– 0·2	2·0	4·4	7·1	9·7	8·4	9·6	7·2	7·3	8·3	4·0	4·2	8·4	– 1·3	9·0	7·9	9·4
Linseed oil .	175·8	0·1	1·5	2·0	3·8	12·3	11·8	13·2	10·4	11·3	11·8	7·9	8·2	12·6	4·5	12·4	14·3	11·1
Cod-liver oil .	171·0	– 0·6	1·1	8·1	10·0	10·9	8·0	10·4	8·0	8·5	10·1	6·8	6·3	11·8	4·3	9·5	6·4	10·8

Livache's Precipitated Lead Test.—The conversion of a drying oil into a solid elastic substance is due to absorption of oxygen. Linseed oil absorbs 14 to 16 per cent. of its weight, and it is easy to directly measure the quantity absorbed by imbibing in the oil a little spongy metallic lead, well washed and dried *in vacuo*, obtained by precipitating a lead salt by a zinc plate; the whole is exposed to air as long as the weight varies; the increase in weight indicates the amount of oxygen absorbed. By this process, when conducted with the necessary precautions, the quantity of oxygen absorbed by any sample of linseed oil may be rapidly ascertained, and, whether a pure oil is being dealt with or an adulterated oil, or an oil already partially oxidised, in all cases it can readily be ascertained whether an oil corresponds with a given sample.

This reaction ought to draw the attention of practical men, because samples are often met with which, although equally genuine, take longer time to dry. Now, the precipitated lead test, it is claimed, indicates the difference in duration of the time taken by the oil for complete oxidation, and thus predicts beforehand the way in which any given oil will dry when applied to an appropriate surface on the large scale.

Process.—One gramme or thereabouts of the precipitated lead is weighed in a tared watch glass, then 0·5 gramme of oil is spotted upon it drop by drop, spacing out the drops that a little dry lead rests between each of them. At the end of 2 days the following results were noted in regard to oils in column 1. The oils in column II. showed no results during the first 2 days. The figures in the column are the increase after a week:—

I. Oil.	Increase, per Cent.	II. Oil.	Increase, per Cent.
Linseed	14·3	Colza	2·9
„ fatty acids	11·0	Sesamum	2·4
Walnut	7·9	Earth-nut	1·8
Poppy-seed	6·8	Rape	2·9
Cotton-seed	5·9	Olive	1·7
Beech-nut	4·3		

Livache's method is described in all textbooks with multifarious proofs. However, there can be no room for doubt that it is far from reliable; moreover, according to circumstances it gives very variable results. This was pointed out as far back as 1888 by A. Cheneorier, whereupon Livache replied that the method only gave correct and comparative results by strict adherence to the instructions.

Jean has tested Livache's method with fish oils in dry air under a bell jar with H_2SO_4, with the following results:—

Oil.	Increase in Weight, per Cent.	Oil.	Increase in Weight, per Cent.
Whale	8·26	Menhaden	5·45
Japanese fish	8·19	Sperm	1·63
Cod-liver	6·38		

Lippert found for linseed, by Livache's method, higher oxygen numbers than given by Livache himself, viz. for fresh raw oil 17 to 18, in one case 19, for aged oil 15 to 16.

Weger tested Livache's method against the same oil on a glass slab by itself, and also on a glass slab with both red lead and litharge as driers respectively. He found that the amount of lead in Livache's method must be increased in order to get a sharp maximum.

Oils.	Increase in Weight, per Cent.		Insoluble Fatty Acids.		Soluble Fatty Acids.		Final State of the Sample after 2 Years.
	After 1 Year.	After 2 Years.	After 1 Year.	After 2 Years.	After 1 Year.	After 2 Years.	
DRYING—							
Linseed	10·3	7·0	44·3	38·2	40·9	50·2	At first dry, becomes slightly viscous.
Walnut	9·4	7·6	44·3	45·4	40·9	37·6	At first dry, becomes slightly viscous.
Poppy-seed	8·0	5·3	51·4	44·4	33·0	42·3	At first dry, liquifies perceptibly.
Cotton-seed	6·3	4·5	61·7	57·6	30·9	31·9	,, ,, ,, ,,
Beech	6·1	5·0	64·4	55·2	25·6	39·1	,, ,, sticks to the finger.
NON-DRYING—							
Colza	6·0	5·3	76·7	69·1	25·6	26·1	Solidified, transparent, sticks to the finger.
Sesamum	5·2	4·8	76·8	68·7	22·2	25·0	Solidified, transparent, sticks to the finger.
Earth-nut	5·7	5·6	72·5	66·6	24·5	29·7	Very thick, but remains viscous.
Rape-seed	5·8	5·4	77·2	75·8	15·6	19·4	Solidified, transparent, sticks to the finger.
Olive	5·3	5·7	73·1	66·2	15·6	28·9	Very thick, but remains viscous.

Conclusions.—A. The oxygen acting on the drying oils, transforming them rapidly into solid products, or on the non-drying oils, slowly turning them rancid, converts a part of the insoluble fatty acids into soluble acids. In the course of time this transformation, of which the extent is proportional to the drying capacity of the particular oil, increases in a continuous way, and the fatty acids after oxidation are changed into homologous acids of lower atomic weight.

B. After two years non-drying oils approached very perceptibly the appearance and composition of drying oils after a single year.

This action is relatively slow under the conditions of the preceding experiments, but the same result would probably be obtained more rapidly if the non-drying oils were placed under conditions in which they could absorb oxygen more rapidly. In certain cases these oils are then converted into solid products.

Bishop's Silica and Rosinate of Manganese Test.—1. Ten grammes of oil are weighed in a capsule, and 2 grammes exactly of manganese rosinate added. The capsule is put into the water-bath, stirring it from time to time until the complete solution of the rosinate, from 5 to 10 minutes being sufficient for this. It is then cooled.

2. One gramme of silica is weighed in a flat-bottom capsule with a little glass stirrer. By aid of a dropping tube, a quantity of oil, as near as possible approaching 1·02 grammes (i.e. 1 gramme of oil plus 0·02 of rosinate), is let fall drop by drop over the whole surface. Both the weight of oil and total weight are noted. The oil is mixed with the silica by the stirrer, so as to have a divided mass, perfectly homogeneous, covering the whole bottom of the capsule. This is left at 17° to 25° C. in the case of drying oils, at 20° to 30° C. for non-drying, and weighed after varying periods; e.g. 6 hours, 16 hours, 22 hours, i.e. 3 times in 24 hours. After each weighing the surface is renewed by agitation with the stirrer. The degree of oxidation is furnished by the maximum increase multiplied by 100 when 1·02 grammes weighed exactly is used. Using pure linseed oil and the same oil with 2 and 4 per cent. of rosinate the following were the results. The linseed oil had a specific gravity of 0·9322 at 15° C., and the temperature ranged throughout from 20° to 25° C.:—

Increase per Cent. at the end of	No Drier Added.	2 per Cent. of Rosinate Added.	4 per Cent. of Rosinate Added.
6 hours	0	12·35	11·10
22 ,,	0·50	15·65	15·50
24 ,,	0·80	15·85	15·30
30 ,,	2·50	16·25	15·30
48 ,,	7·30	15·65	14·90
72 ,,	15·00	14·65	14·10
96 ,,	16·40	15·15	13·60
120 ,,	15·30	14·05	13·20
144 ,,	14·90	13·75	13·20
168 ,,	14·30	13·35	13·20
288 ,,	14·00	13·25	13·10

These experiments decisively showed the energetic action of manganese rosinate as drier, as this salt produced the total oxidation of the oil 3 or 4 times as quickly as in operating with simply divided oil. It also confirms the conclusions of Cloez and Mulder, Bauer, Hazura and Livache on the formation not only of solid products but also of volatile products. If the oxidation is too strong, as when 4 per cent. of rosinate was added, a final result is obtained very much more quickly and at the same time a feebler absorption, this being explained by the formation of a higher proportion of volatile products. In the experiments that follow, therefore, 2 per cent. of rosinate was used:—

TABLE SHOWING THE EFFECT ON DRYING OF FILMS OF LINSEED OIL TREATED WITH 2 PER CENT. OF ROSINATE OF MANGANESE.

Increase per Cent. at the End of	Pure Linseed Oil. Specific Gravity 0·9322. Temperature 17° to 23° C.	Linseed Oil Containing 5 per Cent. of Rosin Oil and 5 per Cent. of Mineral Oil. Specific Gravity 0·9323. Temperature 17° to 23° C.
6 hours	13·50	11·50
22 ,,	16·30	14·80
24 ,,	16·40	14·90
30 ,,	16·20	14·80
48 ,,	15·90	14 60
120 ,,	14·80	13·80

The influence of temperature is very great, and it is well with linseed oils not to exceed 28° C., but above 17° C., so as to effect the oxidation as quickly as possible. The experiments showed also the inferiority of exotic linseed oils of a low specific gravity, and also showed that it is possible to establish by comparison the inferior quality due to clever adulteration.

TABLE SHOWING THE OXYGEN ABSORBED ON DRYING OF FILMS OF VARIOUS OILS TREATED WITH ROSINATE OF MANGANESE.

Oils.	Specific Gravity.	Average Degree of Maximum Oxidation.	Ratio $\frac{17\cdot05}{x}$.
French linseed	0·9327	17·05	—
Linseed from La Plata . .	0·9304	15·20	1·12
Hemp-seed	0·9287	14·40	1·18
French poppy-seed . . .	0·924	14·20	1·20
Commercial walnut . . .	0·924	9·70	1·23
Demargarinated cotton-seed .	0·923	8·45	1·80
Non-demargarinated cotton-seed	0·924	8·60	1·98
Senegal sesamum . . .	0·9215	8·70	1·96
Indian ,, . . .	0·921	7·40	2·30
African earth-nut . . .	0·916	6 70	2·54
White ,, . . .	0·916	6·50	2·62
French colza	0·9142	6·40	2·66
Indian ,, ...	0·9137	5·85	2·91
Olive	0·9155	5·30	3·21

Bishop claimed that the degree of oxidation can therefore be used to control the iodine number, and that in many circumstances it was even capable of replacing it. In fact, he adds, in addition to its great simplicity and the minimum cost of carrying it out, which makes it a very practical method for the industrial laboratory, *this method furnishes very often a more rational and more complete indication than the Hubl number*, as it permits many minor interesting details to be noticed. In consequence, this process serves to fix the value and establish the nature of the identity of an oil, whether taken separately or compared with a type. Moreover, it may be applied in the case of certain mixtures, not only of oils among themselves, but also of commercial products, such as lard and alimentary fats, which often contain very variable quantities of vegetable oils. In this last case, instead of oxidising directly either the melted and clarified fat or the fluid part extracted by pressure, the liquid fatty acids may be operated upon, separated from the solid acids by Halphen's process. The oil is saponified, the soap dissolved in water, and precipitated with acetate of lead. The lead soap is extracted with ether, and the ethereal solution of the lead salts of the non-saturated fatty acids is precipitated with weak sulphuric acid. Indications still more interesting and more precise are obtained by taking the iodine value before and after oxidation. The determination of the degree of oxidation gives results in immediate connection with the value of the oils for certain of their industrial purposes, and, as has been shown, certain falsifications can be detected by the process. Moreover, it will show whether recently crushed or old tanked oil is being dealt with.

TABLE SHOWING WEGER'S EXPERIMENTS IN DRYING LINSEED OIL FILMS BY LIVACHE'S METHOD, AND ALSO AS MADE INTO PAINTS WITH LITHARGE AND RED LEAD RESPECTIVELY.

By Livache's Method. Increase in Weight.		The same Oil Spread on a Glass Slab.	Red Lead Paint Film. The same Oil with 6·6 Grammes of Red Lead to 0·3188 Gramme of Linseed Oil.		Litharge Paint Film. The same Oil with 10·4 Grammes of Litharge to 0·4910 Gramme of Linseed Oil.	
Days.	Increase per Cent.		Days.	Increase per Cent.	Days.	Increase per Cent.
1	11·4	Gave a	1	2·10	1	2·00
2	12·2					
3	12·4	Maximum of	2	11·30	2	11·30
4	12·6					
5	—	17·1	3	14·14	3	13·64
6	12·9					
7	—	on a	4	14·65	4	14·32
8	13·5					
15	14·8	Glass Slab in	5	14·59	5	14·27
42	17·2					
53	18·1	5 to 6 Days.	7	14·05	7	14·21
85	20·4					

Weger found the following oxygen absorption addition figures:—

TABLE SHOWING WEGER'S EXPERIMENTS IN TESTING DRYING OF RAW AND BOILED OIL FILMS WITH THEIR OXYGEN ABSORPTION FIGURES.

Oil.	Days.	Maximum Increase, per Cent.
Rape-seed . .	7	7·6
Olive . . .	20	5·2
Pine-seed . .	29	10·5
Palm kernel . .	13	0·8
Air-blown rape .	15	7·7
Hemp . . .	4-4½	13·4-13·6
Poppy-seed . .	6½	13·4
Wood (various) .	3-9	13·4-15·9
Indian linseed .	4½-6	16·8-17·3
Commercial linseed . . .	4½-8	17-18·7
English linseed .	3½	19·7-19·9
Old tanked linseed	3	15·1-15·7
Indian linseed (heated for a short time at 150° C.) .	6	17·0
Indian linseed blown (cold) .	8	16·7
Indian linseed blown (hot) . .	5½-6½	8·2-9·3
Stand . . .	18	11·1
Thickened . .	18	10·7
Electro boiled .	1½-2	15·1-16·7
Commercial boiled (Hydrated oxide of manganese) .	1-2	14·7-14·8
Commercial boiled (litharge) . .	16-24 hours	14·61-14·8
Boiled linseed prepared with 3 per cent. of rosinate of manganese in the cold . .	24 hrs.	14·7-16
Boiled linseed prepared with 3 per cent. of lead manganese rosinate in the cold . .	—	17·2
The same after 18 months' exposure to the air . .	—	10·9
Boiled rosin oil .	7½	23·3

Weger thus found Livache's method defective. The lead powder increased in weight of itself, therefore this method is unreliable. Moreover, the amount of lead powder prescribed by Livache—ten times the quantity of drier to oil—must be taken; hence 0·2 gramme of oil requires 2 grammes Pb. Again the method is not proof against atmospheric influence, and the weight is not constant for weeks. Yet Livache considered the reaction ended, remained constant once or twice. Between 2 and 20 days the increase in weight is less that 1 per cent., but the weight increases later on. The following table shows the oxygen numbers obtained by Weger:—

Increase in Weight.	English Linseed Oil.	Paint Linseed Oil.	Indian Linseed Oil.	Varnish Oil.
1 day . .	13·7	11·6	11·4	12·3
2 days . . .	14·1	11·9	12·2	13·0
10 " . . .	15·0	12·8	13·8	14·0
53 " . . .	18·9	17·3	18·1	18·3
85 " . .	21·3	20·2	20·4	20·7

Weger tried to replace lead powder by other substances, litharge and red lead.

TABLE SHOWING THE OXYGEN CARRYING CAPACITY OF VARIOUS FINELY DIVIDED SURFACES.

Oxygen No.	Painters' Linseed Oil Alone.	Painters' Linseed Oil on Copper.	Painters' Linseed Oil on Braunstein.	Painters' Linseed Oil on Sea-sand.	Flanders' Linseed Oil on Sea-sand.
1 day .	0·9	9·8	9·4	2·3	1·7
2 days .	1·3	18·0	11·8	1·9	1·4
3 „ .	0·7	18·3	11·1	0·2	0·3
4 „ .	—	17·4	—	—	—

Borries also tested Livache's method. He took, according to original instructions, 1 gramme of lead powder, for 0·2 to 0·4 gramme of linseed oil. In 24 hours he obtained an oxygen number of 13·9, in 51 hours 15·5. He tested a great number of products, zinc dust, chalk, borax, lead chromate, lead peroxide, oxide of iron, powdered wood charcoal, coal dust. They gave almost none or a very slight increase in weight. Copper oxide after 1 day, 2·2; after 5 days, 13·5. Potassium permanganate, after 1 day, 10·4; after 2 days, 11·7; after 5 days, 12·1. After a longer period the permanganate itself changed in weight. Barium peroxide after 24, 48, 56, 72 hours, 14, 14·2, 14·7, 14·6. Manganese borate (left in air until of constant weight), 1, 2, 4, 7 days, 10·5, 11·5, 11·6, 12·3. Platinum black after 1, 2, 4, 6, 7 days, 6·3, 11·2, 13·5, 14·3, 15·0. Braunite 1 day, 15·2; 2 days, 14·4. Lead powder in an atmosphere of oxygen gave no higher results than in air, in 56 hours 16·9, of which 1·6 must be deducted for a blank test. Lead powder and linseed oil in an atmosphere of CO_2 gave only a slight change in weight. Ozonised air gave a perceptible acceleration in one experiment after ¼ hour, 15·45; however, lead itself increased in weight. It is well known in Livache's method the lead acts as a carrier of oxygen to the oil, whilst it is also evident that other substances do not possess this property even when finely divided, yet the carrying of the oxygen of the air is in the ordinary Livache process very circumscribed, but better results are obtained when the air has access to the oil on all sides. This principle seems first to have been recognised by A. Vogel. He drenched cotton-wool with olive oil, and hung the cotton-wool so treated in the air, and found in three months an oxygen absorption of 3·7. Fahrion used pieces of chamois leather, which he soaked with a weighed quantity of oil and hung up in the air. But the highly hygroscopic nature of chamois leather necessitated the determination of its moisture content and also that of the air. This defect is only partially remedied by a blank experiment. The increase in weight after 6 weeks was 11·6 per cent. for linseed oil, thus giving an oxygen number of similar magnitude to Mulder's. Again Mulder emphasises the defect of too thick films, and urges that only small amounts of oil should be used in testing. Yet free linoleic acid even in thick layers, gives higher numbers. In a porcelain basin, tared with a glass rod, 3 grammes of cotton-wool were soaked with 9 grammes linoleic acid, and with occasional turning over, left in the air. The maximum increase in weight, in 8 days was 13·3 per cent. Steenberg used filter paper to subdivide the oil; 0·9 gramme of boiled oil were distributed over a piece 13 cm. long and 11 cm. broad, say 6 to 7 milligrammes per square cm.; the paper was rolled up and left in a test glass on foot, protected from dust under a large cork-stoppered beaker glass. The increase in weight was determined daily. Steenberg made no experiments with pure raw oil. In his boiled oil research, extending over a week, he found oxygen numbers of over 18. However, in a test with linoleic acid separated from soap, therefore partly oxidised, there were found after 1 day, 0; after 3 days, 13·2; and after 5 days, 15·7 per cent. increase in weight. It is not to be denied that the above method does not meet the practical requirements, where linseed oil is mixed with pigments in a thin layer spread over a surface, and under the influence of the oxygen of the air hardens only on one side.

This method of working was correctly known as plate tests, and their chief fault, according to Mulder, was that the film was too thick, yet no one tried to use Mulder's method with thinner films. Experiments in this direction were begun by Weger in 1897, but were held over by a publication of Weger. The latter used tin plates, 18 centimetres long by 10 centimetres broad, weighing 56 grammes. Moreover, 1 centimetre round the plate was left free, the remaining surface was coated with oil, and the plate with oil-free border placed at an angle of 30° for about 10 minutes. The excess of oil collecting at the bottom is removed by bibulous paper and the border carefully cleaned. Then the plate with the oil-free border is placed on the balance and rapidly weighed. The oil, which has been previously removed from the other side, may during weighing flow back; absolute uniformity of the oil film is never attainable. The plate must be carefully cleaned for the test. It must be free from dust, to prevent flaws in the coat, and cracking. The tin plate method requires a room with a uniform temperature, and the plate is protected from dust in a glass case with ventilation holes. The gross weight of the plate is doubtful, so it must be weighed very exactly. On this account, Weger selected aluminium plates. They had the benefit of aluminium weighing but little, 3·5 to 5 grammes, but losing greatly on washing with lye. Finally, Lippert chose glass plates only 2 millimetres thick and 2·5 to 3·5 grammes in weight. He reckoned that the oxygen number was influenced by temperature and other circumstances, and that the method is unfit for comparative tests. The chief critical point is, finally, the moment of the greatest increase in weight. This moment is generally termed the drying-point. Lippert made many tests on boiled oil and obtained oxygen numbers up to 19. If these tests are interesting the fact remains that the lower layer was uninfluenced. But these were much thinner. Mulder prescribed 0·7 and 1·2 per sq. centimetre. Lippert, in his last research, used pure raw linseed oil, which gave the following oxygen numbers:—

1 day	0
2 days	0·5
3 „	1·3
4 „	1·6
5 „	12·6 dry
6 „	14·4
7 „	15·4
8 „	15·4

After 8 days the weight decreased. In this test the drying-point occurred long before the maximum increase in weight. Weger used plates. He attained greater orientation in his experiments and also found greater increase. A paint oil on a glass plate gave the following increases:—

	Per Cent.
After 24 hours	7·0
„ 3 days	14·9
„ 5 „	19·0 dry
„ 7 „	20·6
„ 9 „	20·6

Weger tried to replace glass slabs by lighter material. Gelatine, paper, celluloid, hard gum, were quite unsuitable. Then sheet-metal was less faulty, but the thickness of the coat was not uniform, and the result inaccurate. Mica plates behaved well, but were readily damaged. Weger therefore went back to glass plates; their weight was about 25 grammes, the measurement of the coated surface was 80 sq. centimetres, the weight 25 to 70 milligrammes, therefore 0·3 to 0·9, on an average 0·4 to 0·6, milligrammes per sq. centimetre. Hence 0·1 milligramme more or less on 0·4 to 0·14 per cent. of the used oil speaks for itself; therefore a good balance is necessary above all things. Any trace of dust is to be avoided, and the plate must be scrupulously clean; when it is not left long enough in the balance case, errors may occur in weighing, also if before weighing it be rubbed with a cloth.

Temperature hastens the rapidity of drying and increases the weight due to oxygen absorption. The same oil in cold, cloudy weather gives a different increase in weight from bright warm weather; the higher the temperature the less is the increase in weight, although more volatile matter escapes. The longer an oil takes to dry, the greater is the necessity to repeat the test. The chief difficulty rests in the fact that the correct maximum increase in weight has to be guessed. Sometimes it happens that the correct increase in weight remains constant for 12 hours or for several days. In other cases, a very rapid increase in weight occurs. Chemical equilibrium, according to Mulder, is attained by this end; increase is generally never attained until the change in weight shows no more true increase in weight. The hard drying of the film—that is, the moment when it resists a strong pressure of the fingers—is, with the maximum weight, spoken of as the drying of the film which light pressure with the finger no longer affects ½ to 1 day earlier. By hard drying Weger means, however, the outer half of the film. Weger concluded that the average oxygen absorption number of linseed oil was 18 per cent., and that seems correct, as Mulder found 17·1 and 18·1. Weger expressed the result of the drying process graphically; the time formed = the abscissæ, the increase in weight, the ordinates. The experiment with Indian linseed oil gave

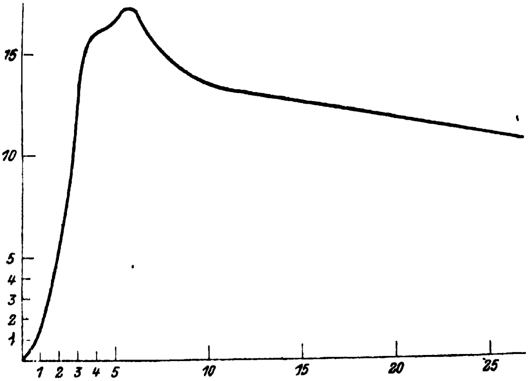


FIG. 76.

All these curves at first form a gradual, then long continuous rapid rise, then a gradual maximum, a longer or shorter stay at this height, then a seemingly abrupt fall, and in the end a continuous slow fall.

Weger found lower figures than Mulder, but at 18° filtration linoleic acid still contained solid fatty acids, whilst Mulder's was prepared by the Warrentrapp method, or long cooling of the alcoholic solution freed from fatty acids. Finally, Weger subjected linoleic acid without treatment to oxygen absorption and thus prevented any partial autoxydation.

TABLE SHOWING THE OXYGEN ABSORPTION OF THE MIXED FATTY ACIDS OF LINSEED OIL.

Oxygen Absorption.	Commercial Linoleic Acid.	The same Linoleic Acid Filtered at 18° C. from the Solid Remainder.
1 day . . .	9·6	14·5
1½ days . . .	10·9	—
2 " . . .	—	15·2
2½ " . . .	11·5	—
4 " . . .	—	14·4
4½ " . . .	11·9	—
5½ " . . .	13·0	—
6 " . . .	—	15·6
6½ " . . .	14·0	—
7½ " . . .	14·4	—
8 " . . .	—	14·4
15 " . . .	13·4	—
21 " . . .	13·4	—
25 " . . .	—	15·6
29 " . . .	—	15·6
48 " . . .	13·6	—
60 " . . .	—	12·8

Driers.—Weger's assertion that manganese and lead alone acted as driers, was extended by Meister to all metals, but especially to the two first, and cobalt driers after 50 years have again come into use. Again a certain metal content gives a maximum result, and these maxima are with different metals proportional to their molecular weight. He tested 17 metals in that way; the precipitated rosinate was prepared, and 2 per cent. of the dried preparation dissolved in three-months' old La Plata oil at 150° C. (302° F.) and the boiled oils so obtained were tested on glass slabs for their oxygen absorption in 12 hours and time of drying. The results gave the following grouping:—

TABLE SHOWING FOR THE METALS WHOSE SYMBOLS ARE GIVEN THE TIME OF DRYING IN HOURS, AND THE PERCENTAGE OF OXYGEN BY WEIGHT ABSORBED IN 12 HOURS BY FILMS OF LINSEED OIL, CONTAINING IN SOLUTION 2 PER CENT. OF THE RESPECTIVE METALLIC ROSINATES.

Metal.	Time of Drying, Hours.	Absorption per Cent. by Weight	Metal.	Time of Drying, Hours.	Absorption per Cent. by Weight.
Mn. .	12	17·4	Ni	77	8·1
Pb . .	26	9·4	Al	76	4·7
Zn . .	30	6·5	Mg	85	2·8
Ca . .	32	6·0	Ba	86	2·4
Co . .	36	5·9	Sn	87	2·6
Cu . .	46	4·9	Cr	95	2·0
Fe . .	60	4·1	Hg	115	1·7
Sr . .	75	2·9	Bi	117	1·8
Cd . .	76	4·7	Raw Oil	121	0·93

The results with Hg and Bi are not quite reliable, as during solution of the mercury-rosinate a portion of the mercury was volatilised, and much bismuth-rosinate did not dissolve completely in the oil. The driers with (*a*) lime and (*b*) zinc rosinates are the most interesting, as both these bodies, first by Chevreul, and then by Mulder, and latterly by Weger, were denounced as driers. Attempts to use fused precipitated zinc-rosinate prove it most intractable.

Comparative Increase in Weight due to Oxygen Absorption of (a) Linoleic Acid without a Drier, (b) with Drier.—More recently Fahrion made two parallel experiments, one with linoleic acid pure and simple, the other with linoleic acid in which a certain percentage of lead linoleate was dissolved, so that the lead content equalled 1 per cent. Pb. In two porcelain basins, tared with a glass rod, 3 grammes of cotton-wool were saturated with about 9 grammes of linoleic acid, and allowed to stand at summer temperature. The basins were weighed daily at the same time, with the following results:—

TABLE SHOWING INCREASE IN WEIGHT DURING DRYING OF (*a*) LINOLEIC ACID ALONE, (*b*) LINOLEIC ACID CONTAINING 1 PER CENT. Pb.

	Without Drier.		With Drier.	
	Grammes.	Per Cent.	Grammes.	Per Cent.
Weight of the linoleic acid	8·877	—	9·278	—
1 day increase in weight	0·012	0·1	0·119	1·3
2 days ,, ,,	0·048	0·5	0·519	5·1
3 ,, ,, ,,	0·282	3·2	0·956	10·3
4 ,, ,, ,,	0·694	7·8	1·233	13·3
5 ,, ,, ,,	0·879	9·9	1·356	14·6
6 ,, ,, ,,	1·006	12·0	1·416	15·3
7 ,, ,, ,,	1·160	13·1	1·416	15·3
8 ,, ,, ,,	1·181	13·3	—	—
9 ,, ,, ,,	1·161	13·1	—	—

Ethylic "linoleate," the combination of the ethylic esters of the fatty acids of linseed oil, prepared by partial saponification, was tested for its oxygen absorption, using aluminium plates. The following results were obtained:—

TABLE SHOWING COMPARISON OF OXYGEN ABSORPTION OF LINSEED OIL AND OF ETHYL LINOLEATE MADE THEREFROM.

Oxygen Number.	Linseed Oil.	Ethyl Linoleate.
After 1 day	0·8	2·0
,, 2 days	2·7	3·7
,, 3 ,,	7·6	6·2
,, 4 ,,	13·5	9·0
,, 5 ,,	16·3	10·8
,, 6 ,,	16·55	12·4
,, 7 ,,	Decrease	13·6
,, 8 ,,	—	13·6
,, 9 ,,	—	Decrease

As a sequel to Borries' work, Genthe started a series of researches to estimate the true oxygen number. Discarding plate tests, he always used a known thickness of film. In spite of this Genthe never appears to have differentiated between the true and the apparent oxygen number. His experiment was as follows: A piece of filter paper 10 centimetres wide, 30 centimetres long, was folded and bound together by glass and india-rubber bands. The diffusing distributor so obtained was coated with linseed oil, 0·300 gramme, therefore 1 milligram per sq. centimetre, and laid in a flask of 1200 cubic centimetres capacity with aluminium hydrate, hung from hook attached to the stopper. The volatile decomposition products were absorbed by solid KHO or by asbestos-divided caustic potash lye. A monometer passed through the perforated stopper and paraffin oil used as indicating fluid. In a second flask a blank experiment was conducted without paraffin oil. The reaction was represented graphically, the time as abscissæ, and the cubic centimetre of paraffin oil as ordinates. The curves assumed the S form. At the close of the reaction there was always a long but uniform oxygen absorption, then the curve finally passes into a straight line. Instead of air, oxygen was used, so that the reaction was hastened only to a small extent. By covering the flask, in broad daylight, with black paper, the reaction first started in 18 to 20 days, and ended in 50 days.

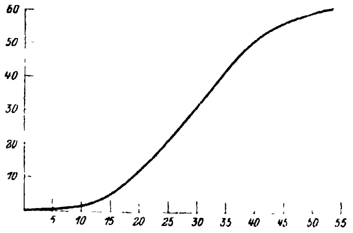


FIG. 77.

A similar experiment was made without using potash and gave a corresponding result, only the ordinates were 10 per cent. smaller. It must not be forgotten, therefore, that the true oxygen number is only 10 per cent. higher than the apparent. Of the substances, volatile at the ordinary temperature, only CO_2 entered into Genthe's experimental results, and many of these, in Mulder's experiments, formed one-fifth to one-sixth of the total volatile substances.

In broad daylight the reaction sets in well by the second day and lasts 8 to 10 days, sometimes more; under the circumstance of the experiment 3 to 7 days; readings were taken morning and evening, the small oxygen number during the night is shown in Fig. 78.

The different natural illumination of different days gave different

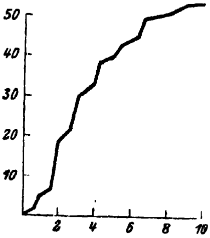


Fig. 78.

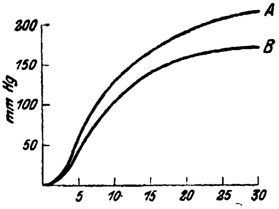


Fig. 79.

results. Genthe chose artificial light, the light of the mercury vapour lamp, which consists chiefly of blue-violet and ultra-violet rays. It accelerates the reaction greatly. The two curves A and B shown, Fig. 79, represent two experiments with 0·3 gramme linseed oil and 250 c.c. oxygen. Drying occurred in 24 hours, and omission of KHO from later experiment did not affect second result, whilst the action of the latter at higher temperatures was to be seen. This gives the result at 95° in Uviol light, A in oxygen with KHO, B in air with KHO, and C in air without KHO; Fig. 80, generally the reaction through the increasing of the temperature was strongly accelerated, that the absorption in pure oxygen is considerably higher than in air. Whilst curves in the first 80 minutes are about equal, C from thence onwards proceed in a horizontal line, whilst th

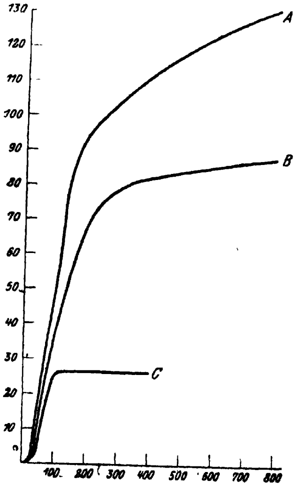


Fig. 80.

pressu
volatile . remains constant. This shows that from that point muc
doubtful wtter is given off, also oxygen absorbed, and finally it i
From thher in the above results no volatile matter was formed
number of ea rves a direct comparison with the apparent oxyge
writers cannot be made, so that Genthe from th

volume of the oxygen absorbed has calculated the weight of the latter. He found on an average for the true oxygen number—

In diffused daylight	22·6
In Uviol light at ordinary temperature	25·8
„ at 95° air	26·5
„ at 95° O	34·7

It has been seen that Weger calculated the figure as 43·7, and in ordinary light found the apparent oxygen number as 18, nor was 25 per cent. over-estimated. Genthe himself notices the great difference and that the oxygen numbers of linseed oils are strictly comparative matters. It becomes necessary, therefore, to show how the operation is conducted and how the course of the S curve receives the straight line of the combustion curve. Genthe's Uviol experiments are approached by Weger's. In these three experiments the filtering substance and the caustic potash as a solution in asbestos in small basins intervened.

	I.	II.	III.
Increased weight of linseed oil	0·053	0·051	0·055
„ „ KHO	0·048	0·038	0·042
Total	0·101	0·089	0·097
Weight of the oxygen calculated from the volume	0·099	0·090	0·093

The agreement between the two first experiments is very good and shows the proper working of the Genthe tests. As during the former tests 0·300 gramme of linseed oil was taken, this fact comes out strongly in the oxygen numbers of the tests.

Comparison of the first series of apparent oxygen numbers with those of the third series where the oxygen number was calculated from the

	I.	II.	III.
Apparent oxygen number	17·7	17·0	18·3
True „ „	33·7	29·7	32·3

The agreement of the apparent O number with the average Weger number 18 is quite satisfactory, and the true O number makes it evident that Weger's calculated value is too high. However, Genthe's results do not coincide with practice, as in the last case the atmospheric pressure varies, whilst in Genthe's experiments the pressure remains constant.

Ozone Absorption of Oils.—As a sequel to the oxygen absorption the ozone absorption of oils may be briefly described. Air containing ozone acts on linseed oil. Genthe also found the presence of ozone in his researches.

The Ozone Value of Linseed Oil.—Borries passed ozonised air through a glass tube over a film of linseed oil and lead in powder and found the maximum increase in weight to be 14 per cent. However, Molinare and Soncini found a greater increase in weight, viz. 30 per cent., as the result of passing ozonised air into linseed oil direct. On condition that all the double links were saturated by the ozone molecule, they calculated for the iodine value of 171 the ozone value of the same linseed oil as 32·3. G. Fenaroli estimates the ozone value of linseed oil thus: He dissolves the oil in petroleum ether and transfers the solution into a Liebig's potash bulb, and then passes a stream of ozonised air or oxygen at the rate of 180 bubbles per minute at a temperature not exceeding 40° C. until saturated. In this way he found the ozone value of 34. Harries suggested O_4 instead of O_3, and the formation of a double bond. On the other hand, the energetic oxidation of ozone cannot very well be accepted, as no volatile products are formed in the reaction in question, and there is nothing to show that the ozone is not absorbed as ordinary oxygen. On this point only the analysis of the ozonides and the oxyacids can throw any light.

The Chemistry of the Reactions that Occur During the Drying of Linseed Oil.—Mulder's work long remained practically unknown.

Linoxin.—It was known that dried oil did not melt on heating, but charred, that it was then only very partially soluble in ether (15 per cent. Schubarth), and that it dissolved in caustic potash lye. Mulder examined the subject by the aid of coatings on tin plates or on glass plates; after being left 3 to 4 months in the air, the dried skin was exhausted with ether which dissolved out the under layer.

Action of Solvents on Linoxin. Properties of Linoxin—It was thereafter, treated with ether, alcohol, and water, and the residue, termed linoxin by Mulder, was dried over H_2SO_4. Mulder obtained linoxin as a solid white amorphous mass, more or less elastic like leather or gutta-percha, heavier, and insoluble in water, alcohol, and ether. It is also insoluble in chloroform and carbon disulphide, but swells greatly therein. On digestion with a mixture of alcohol and chloroform it passes into solution. In turps it becomes resinous, but does not dissolve. In caustic potash it dissolves with a red colour. In ammonia it dissolves on long boiling.

Action of Heat on Linoxin. Liberation of Acrolein.—On heating it is coloured red and gives off a piercing odour of acrolein, which is due to the combustion of the free linoleic acid, and is not produced from the glycerine. The combustion of linoxin (Mulder) gave the formula as $C_{32}H_{54}O_{11}$, and on the dry distillation of linseed oil linoleic acid anhydride, $C_{32}H_{54}O_3$, was obtained, so he regarded linoxin as the oxidation product of the anhydride of linoleic acid. He assumed that the dried oil (*a*) first split off the total glycerine, (*b*) that the solid fatty acids, and (*c*) the oleic acid remained unchanged, and were dissolved during the treatment of the dried film of il with ether. About 20 per cent. so dissolves. Finally the linoleic acid gave off water and then absorbed oxygen. The results of the following experiment by Mulder confirmed his belief and the soundness of his views :—

Lead Linoleate. Its Composition and Properties.—He placed an ethereal solution of lead linoleate on a glass plate; on spontaneous evaporation of the ether a white film was obtained, becoming transparent in a few hours, and drying hard in a day. So as to weigh them the films were removed from the glass and dried over H_2SO_4. Analysis gave $(C_{16}H_{27}O_5)_2Pb$. The free linoxic acid, $C_{16}H_{26}O_5$ or $C_{32}H_{52}O_{10}$, is differentiated from linoxin only by 1 molecule of water. In another experiment lead linoxate was exhausted with ether, 10 per cent. dissolved (lead oleate in Mulder's opinion). The combustion of the insoluble lead salts gave for the corresponding acid $C_{32}H_{50}O_9$, which Mulder described as the anhydride of linoxic acid.

Linoxic Acid.—Free linoxic acid was prepared from the above lead salts by decomposing the salt suspended in alcohol by H_2S, filtering and precipitating with water as a pure white substance, which changes to a colourless resinous mass. The acid can, in no circumstances, be crystallised; on heating it becomes blood-red. On treatment with aqueous KHO or NaHO, the red coloration appears in the cold in white "linoxic acid," also dissolves in ammonia, and this solution becomes slightly coloured on boiling. The lime salt is insoluble in water and melts under 100° C. The magnesium salt readily dissolves in cold alcohol. The red product was, by Mulder, distinguished from the white as red linoxic acid.

White Linoxic Acid.—Another linoxic acid was obtained by the autoxidation of free linoleic acid exposed on glass plates for the air to act on it, until it showed no further increase in weight. The oxidation product was colourless, transparent, tacky, resinous. The oxygen absorption number was 17·5 to 19·7. Combustion gave $C_{16}H_{28}O_6 = C_{32}H_{56}O_{12}$. Mulder believed he had obtained a hydrate of white linoxic acid. From the formula he calculated the oxygen absorption number of 25·4, from which, deducting for oleic acid, the numbers found became 22·6, which he accounted for by a slight oxidation.

Red Linoxic Acid.—Mulder states that the above acid loses 6 per cent. of water, on the water-bath becoming blood-red. The combustion of the red linoxic acid so obtained gave $C_{32}H_{52}O_{10}$. On heating at 110° C. this acid gave no water, but on boiling lead linoxate with dilute HCl, red linoxic acid is obtained of the formula $C_{32}H_{50}O_9$, solid at the ordinary temperature, but soft and readily fusible, insoluble in water, soluble in alcohol and ether, with a red colour and an acid reaction. Mulder sought for a red linoxic acid which he could further examine, and thought he obtained it thus. It was spread on glass in a thin layer, and after frequent treatment with ether placed in the open air 19 days. It was nearly colourless, and gained 6 per cent. in weight, that is about as much as the white linoxic acid lost in the water-bath.

Red Linoxic Acid from Linoxin.—Finally, Mulder, and that was the corner-stone of his theory, obtained red linoxic acid from linoxin. He dissolved linoxin in KHO, precipitated the solution by HCl, dissolved the precipitate in alcohol, and dried the residue by evaporation at 100° C. Combustion gave $C_{32}H_{52}O_{10}$. Mulder thought that the linoxin, under the action of KHO, eliminated water, changing without bye-products into red linoxic acid. He therefore decomposed the solution in KHO by dilute H_2SO_4, and distilled the filtrate from a retort. The distillate contained only traces of acids, the contents of the retort separated on concentration into red flocks of linoxic acid, leaving on evaporation only K_2SO_4.

Mulder Overlooked the Glycerine now Known to be Present in Linoxin.—Mulder here overlooked the glycerine which linoxin contains in considerable amount, and which, in this case, must at least partially distil. We know how impossible it is to recognise that an anhydrous body such as linoxin could split up on treatment with aqueous potash, the contrary is more likely. The conclusion of Mulder's theory is the presumption that white linoxic acid changes to linoxin. It is to be observed that the former is tacky and oleoresinous at first; when it has been months in the air it dries completely, and, according to Mulder, it passes by elimination of water into linoxin.

Collectively Mulder believed he had handled not only linoleic acid but also the following derivatives therefrom :—

Linoleic acid	$C_{16}H_{28}O_2 = C_{32}H_{56}O_4$
Linoleic acid anhydride	$C_{32}H_{54}O_3$
Red linoxic acid I.	$C_{32}H_{50}O_9$
" " II.	$C_{16}H_{26}O_5 = C_{32}H_{52}O_{10}$
White linoxic acid	$C_{16}H_{28}O_6 = C_{32}H_{56}O_{12}$
Linoxin	$C_{32}H_{54}O_{11}$

The white and the red linoxic acid have the same composition, but a different constitution. To explain the different proportions of water such often occurs with resin acids, and above all things, it is not evident that an amorphous acid can contain water in various stochiometric proportions. In reality, Mulder's formula is incorrect, and the above substances are mixtures pure and simple.

Mulder's Theory of the Splitting-off of Glycerine being the first State in the Drying Process.—Mulder concluded that the first phase of the drying process is the splitting-off of glycerine. Dried linseed oil was shaken up with ether, 21·1 per cent. dissolved, of which 0·5 per cent. dissolved in water. The substance was amorphous, acid, and non-volatile. It gave a soluble lead and barium salt, and reduced Fehling's solution when warmed. Mulder regarded it as glyceric acid

$$CH_2OH \,.\, CH\ OH \,.\, COOH$$

but states that its quantity was small for such an experiment. The water-insoluble residue was pure white, at the ordinary temperature semifluid, partially soluble in cold alcohol, completely so when hot, also in aqueous soda. Solid fatty acids crystallise out of the alcoholic solution on cooling. In the air the above residue did not dry, with KHO did not turn red, proving the absence of linoleic acid. The lead salt was partially soluble in ether. Oleic acid from the decomposition gave pure white fatty acids crystallisable from alcohol.

Glycerine first Split-off from Oleic Acid (Mulder's Theory).—Mulder believed from the following experiment that the splitting-off of glycerine begins with the linoleic acid, whilst the oleic acid and the solid fatty acids are liberated later. Linseed oil was left on glass plates only long enough for a skin to begin forming. The partially oxidised linseed oil was shaken up with ether, the residue on evaporation was completely insoluble in aqueous soda, whilst the oleic acid and the solid fatty acids abounded in glycerine.

Acrylic Acid.—With warm water the above residue left a product volatile in steam, reducing Fehling's solution which Mulder described as acrylic acid, $CH_2 . CH . COOH$.

Glyceric Acid.—In the distilling flask it left a small quantity of an uncrystallisable acid, probably glyceric acid. On the basis of his experiments Mulder concluded that during the process of drying undergone by linseed oil the following changes occurred:—

1. *The Oxidation Products of the Liberated Glycerine. Glyceric and Acrylic Acids.*—First of all the glycerine is split off and oxidised first into glyceric and acrylic acid, and later on, into acetic, formic, and carbonic acids.

2. *Partial Oxidation of the Free Oleic Acid, Palmitic and Myristic Acids Inert.*—The free oleic acid is oxidised to a small extent, whilst the palmitic and myristic acids remain completely unchanged, and partially render the linoxin softer and greasier.

3. *The Elimination of Water and Absorption of Oxygen by Free Linoleic Acid.*—Lastly, the free linoleic acid splits off water, and absorbs oxygen.

The Glycerine Content of Linseed Oil. Glycerine Rest.—This theory agrees at the point where it intersects Mulder's oxygen absorption number of 11·1. He gave the glycerine content of linseed oil, $C_3H_8O_3$, as 8·2 per cent., of which 80 per cent. existed as linoleic triglyceride. The linoleic acid was therefore made out to be 76 per cent. Now taking the passage of the linoleic acid anhydride, $C_{32}H_{54}O_4$, into linoxin, $C_{32}H_{54}O_{11}$, the true oxygen absorption of 26·3, say for 76 per cent. 20. Deduct from that the loss of glycerine 8·2 per cent., and we get the oxygen number of 11·8. At the present day the calculation contains two errors, one with the glycerine residue, C_3H_5, of 4·3 per cent., the other concerns the water of hydration, for which 3·6 should be deducted.

The Final Stage of the Oxidation of Linseed Oil and Consequent Disappearance of Film.—On the completion of the above-described oxidation process (as described by Mulder) a period of chemical rest ensues, whence the oxidation passes into its second stage, not investigated by Mulder. He imagines it, however, to proceed thus. The oleic, palmitic, and myristic acids are oxidised to volatile substances and the remaining coat breaks up. Lastly the linoxin follows suit, and is completely volatilised by oxidation and the film vanishes completely.

Bauer and Hazura's Researches Modify Mulder's Theories.—Mulder's theories remained unchallenged for 20 years, until revised by Von Bauer and Hazura on the basis of their work on linseed oil fatty acids, and by the aid of the methods of fat analysis described meanwhile. They then made the following general remarks :—

The drying of oils consists in the absorption of oxygen and of all liquid oils, only the fluid fatty acids of oleic acid are non-drying, so it may be stated that the more slowly an oil dries the more oleic acid it contains. Finally it is obvious that linolenic and isolinolenic acids, $C_{18}H_{30}O_2$, which contain six free valencies will absorb more oxygen than linoleic acid with only four valencies. An oil will dry better therefore the more the acid $C_{18}H_{30}O_2$ predominates. Finally an oil will naturally dry more slowly the more saturated fatty acids it contains. It is found in actual practice that an oil dries better the higher its iodine value. The experimental testing to confirm Mulder's researches provided the following information—that the red linoxic acid, prepared from Mulder's lead linoxate, has still an iodine value of 61·4 and is in nowise the end-product of the autoxidation. Through free linoleic acid, separated by Warrentrapp's method, a strong current of air was passed. It became a very thick fluid still showing the iodine number of 38·5. The oxidised oil was acetylated. It gave the acetyl No. of 184·6. The oxidised oil was finally exposed to the air in a thin layer at 40° C. for 3 weeks. It was still tacky. The experiment was carried on at 80° C. for a week. The linoleic acid was by this time completely solid and no longer soluble in ether. However, it dissolved readily in KHO, and the solution gave, with H_2SO_4 a yellow precipitate, which readily dissolved in ether. From the above experiments the following conclusions were drawn :—

1. *The Oxidation of Drying Oils does not Consist in Saturating the Free Valencies by Oxygen, but Oxygen is Interpolated Between C and H, and the Oxidation Product so Formed which Contains the Alcoholic OH Group.*—Hence Mulder in his white linoxic acid ound a minimum of 61 per cent. C, so it is to be presumed that the oxidation of linolenic acid proceeds so that, first, three oxygen atoms, of he three double bonds, are unsaturated and that then two oxygen atoms are absorbed; for a pentaoxy linolenic acid, $C_{18}H_{30}O_7$, 60·4 per cent. C is calculated. Between the oxidation of the dried oil acids and heir salts there is no demarcation. The above-described behaviour of linoleic acid, during drying, can only be explained by the formaion of anhydrides; what shape this formation of anhydrides takes cannot be determined preliminary. Hence, oleic acid by the action

of air leaves no solid oxidation products, so it may be taken that in the drying process only linoleic acid, $C_{18}H_{32}O_2$, and linolenic acid, $C_{18}H_{30}O_2$, take part. Further, Bauer and Hazura do not believe that it gives a red linoxic acid, resulting from the molecular aggregation of the white, but that by the action of alkalies or high temperatures, a small quantity of the so-called white linoxic acid is decomposed, and the decomposition product yields the red colour. The preparation and testing of Mulder's linoxin was prepared according to Mulder's instructions, dissolved in KHO, and the solution warmed with H_2SO_4. The acids so separated were syrupy, but soluble in alcohol and ether, and still gave the iodine number of 29·1. The filtrate was agitated with ether, neutralised with caustic potash, and evaporated on the water-bath. The residue was a syrup disseminated with crystals of K_2SO_4. It was shaken with absolute alcohol which left behind a thick brown syrup with a peculiar sweetish taste, insoluble in ether, readily soluble in water. It was recognised by further tests as glycerine, it amounted to 5 per cent. of the linoxin. Therefore, linoxin is not, as Mulder asserted, an acid anhydride, but a glyceride, the oxidation of which is incomplete. The glycerine is only partially split off and oxidised, probably only such as is combined with oleic acid, and solid fatty acids, which in the form of their glycerides absorb oxygen. Instead of linoxin Bauer and Hazura substitute oxylinolein; it is known as such, but the name is not adopted.

Autoxidation Products of Linoleic Acid.—Experiments on the autoxidation product of linoleic acid were not instituted by Bauer and Hazura.

The Preparation of Oxyacids from Oil Oxidised by Subdividing Medium.—However, W. Fahrion has examined this question more closely, as he found a medium for separating the oxyacids from the unoxidised portion in petroleum ether. A linseed oil, oxidised by means of a subdividing medium prepared for comparison with a polymerised oil but not analysed, was saponified, and the mixed acids were separated and treated with petroleum ether. The oxyacids remained behind as apparent thin fluid red oils, a combustion of which gave the following:—

ELEMENTARY ANALYSIS BY FAHRION, OF OXYACIDS PREPARED BY HIMSELF.

	C.	H.	O.	C : H.
Found	69·74	9·84	20·42	18 : 3·05
Calculation for $C_{14}H_{30}O_4$	69·68	9·68	20·64	18 : 3·00

Hence the oxidation had not yet gone far, so it can be presumed that the surrounding linoleic acid is not attacked, only the red oil being a split off, derivative of linolenic acid. The combustion figures correspond well with dioxylinolenic acid, $C_{18}H_{30}O_4$.

The Preparation of Oxidised Oil. Its Properties.—As the red oil was scarcely heated, so a partial saturation of the double bonds by oxygen is probable.

The Preparation of Oxyacids from Oxidised Oil.—In a second experiment the oxyacids were prepared from an oxidised oil, the analysis of which has been already given. This time it was a thick, deep red oil, completely soluble in alcohol and ether. The ammoniacal solution was only partially precipitated by $BaCl_2$, and the insoluble barium salt was decomposed by HCl, the separated acid I. was only partially soluble in ether; soluble portion Ia., insoluble portion Ib. Also the acids from the insoluble barium salt were only partially soluble in ether; IIa. the insoluble portion; IIb. was so but slightly; Ia. and IIa. were thick deep red oils; Ib. a tacky syrup, and IIb. an amorphous brown powder. The following analyses giving the combustion results are the mean of two estimations:—

ELEMENTARY ANALYSES WITH IODINE NUMBERS BY FAHRION
OF OXYACIDS PREPARED BY HIMSELF.

	C.	H.	O.	C : H.	Iodine Number.
Ia.	67·44	9·13	23·43	18 : 29·2	38·3
Ib.	65·84	8·85	25·31	18 : 29	32·3
IIa.	64·19	8·35	26·96	18 : 29·8	30·2
Calculated for $C_{18}H_{30}O_4$	69·68	9·68	20·64	18 : 30	163·2
,, ,, $C_{18}H_{30}O_6$	63·16	8·77	28·07	18 : 30	74·0

The figures C and H lie apparently between di- and tetra-oxylinolenic acid. As to the ratio C : H it follows that, besides an absorption of oxygen, water is also given off. In face of the OH group present, such is very probable. It seems partially to occur with the baryta salts, the partly insoluble in ether is hardly to be explained otherwise. The iodine number lies far below the calculated numbers, which is explained by polymerisation.

When it is possible to obtain a higher oxidation product of linolenic acid it is done without the use of subdivided linseed oil. The oxyacids were partly separated. They were only partially soluble in ether, the soluble portion formed a thick dark red oil, the insoluble an amorphous brown mass, which on analyses gave the undernoted figures. For comparison, the Mulder combustion with the lowest C content, white linoxic acid, is placed parallel:—

FURTHER ANALYSES OF OXYACIDS BY FAHRION CONTRASTED WITH MULDER'S WHITE LINOXIC ACID.

	C.	H.	O.	C : H.	Iodine Number.
Ether insoluble oxyacids .	60·59	7·64	31·77	18 : 27·2	39·8
Mulder's white linoxic acid	61·0	9·3	29·7	18 : 33	—
Calculated for $C_{18}H_{28}O_7$.	60·67	7·87	31·46	18 : 28	0

The ratio of the C to H, in Mulder's figures, points to the acid containing abundant hygroscopic water. The figures found by Fahrion are doubtless inverted by a previous splitting off of water. Hence the figures pertaining to an anhydro derivative

$$C_{18}H_{30}O_8 - H_2O = C_{18}H_{28}O_7,$$

so it is to be concluded that the belief of Hazura and Bauer in a pentaoxylinolenic acid, $C_{18}H_{30}O_7$, being the end product of oxidation, is wide of the mark. Moreover, the latter goes far beyond hexalinolenic acid, and therefore the acids under examination were scarcely homogeneous, and still absorbed iodine. As will be pointed out further on, still higher oxidation products are possible. The more linoleic acid is finely divided, the more readily is its autoxidation brought about. This is best shown by means of cotton-seed oil which, according to Hazura and Grüzner, contains no linolenic acid, only oleic and linoleic. Naturally it takes longer to oxidise than linseed oil. It requires a longer time or a higher temperature. In the same way as linseed oil cotton-seed oil was oxidised, and four different oxylinoleic acids separated as more or less thick dark red oils. Analyses gave the following:—

THE ULTIMATE COMPOSITION OF FOUR DIFFERENT OXYLINOLEIC ACIDS FROM COTTON-SEED OIL.

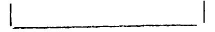
	C.	H.	O.	C : H.	Iodine Number.
I.	70·69	9·91	19·40	18 : 30·3	41·9
II.	67·06	10·00	22·94	18 : 32·2	35·3
III.	64·39	9·54	26 07	18 : 32·0	32·6
IV.	65·85	9·65	24·50	18 : 31·6	22·1
Calculated for $C_{18}H_{32}O_4$ . .	69·23	10·26	20·51	18 : 32·0	81·1
,, ,, $C_{18}H_{34}O_6$ . .	62·79	9·30	27·91	18 : 32·0	0

The ratio C : H shows that the oxyacid I. had split off much water, possibly due to the higher temperature in the oxidation of the oils. If we take the figures for the ratio C : H = 18 : 32, we find that those for the oxyacids II. are almost equal. It leaves, therefore, the combustion results between di- and tetra-oxylinolenic acid. It is naturally very difficult from the combustion results and the iodine value of oxylinoleic and oxylinolenic acid to come to any definite conclusion. The theory as to polymerisation and the splitting-off of water is dealt with later on. The fact that iodine is still absorbed together with the combustion results gives rise to the further theory: That the saturation of each of the double bonds of linolenic and linolic acid is accomplished by successive oxygen absorption and that one of the double bonds of linolenic and linolic acids are indifferent to the oxygen of the air, and only affected by polymerisation. The proof of this theory is still wanting.

Now as various micro-organisms were found in poppy-seed oil, it may be that these minute organisms play a certain rôle in the drying of the oil. In that respect, R. Kissling showed that heating to 120° C. and the addition of phenol stopped the absorption of oxygen. In regard to the second stage of the process of drying, some ideas of W. F. Reid are quoted. He placed some linseed oil skins in the air for 2 to 5 years. In that time Reid claimed the linoxin passed into a thick fluid, which Reid termed superoxidised linseed oil. It is apparently dark coloured, heavier than water, almost completely soluble in alcohol, very acid, forming with basic colours solid salts. Besides, during the weathering and decay of outdoor paint, it plays a special rôle. Unfortunately Reid's oil skins were evidently only half dry and no useful deduction can be made.

Henriques experimented on the readily oxidisable ethyl linoleate. The great rise in the saponification number during autoxidation Henriques explained as due to the splitting up of the molecules with formation of smaller molecules of fatty acids. That this splitting up was due to autoxidation he regarded as improbable, owing to the slight increase in the acid number. He ascribes it to saponification, chiefly on the ground that previously, in the treatment of aromatic alcohols, e.g. the cinnamic alcohols, $C_6H_5 . CH : CH : CH_2OH$, by saponification with alcoholic potash, he had obtained saponification numbers. He was then able to isolate from cinnamic alcohol a yellow, amorphous resinous mass, which contained benzoic acid in small quantity, but chiefly consisting of aldehyde and ketonic bodies. Henriques treated both fresh and oxidised ethyl linoleate in the warm, with phenylhydrazin diluted with acidulated water, and agitated the solution with ether. The evaporated residue was in the first case N. free, and in the second case nitrogeneous. Henriques concluded that during the autoxidation of the esters, first OH groups were fixed by the double bonds and were then changed into ketone groups, or by splitting off yielded aldehydes. Henriques came to another result with the autoxidation product of abietic acid. This acid is known to form the principal portion of rosin; its formula being $C_{20}H_{30}O_2$ is at the present day well established, also that it contains two double bonds. It is therefore the aromatic analogue of linolic acid. It behaves similarly during autoxidation, and is, moreover, also insoluble in petroleum ether. The petroleum ether insoluble oxyabietic acid is present in varying amount in rosin itself, and Henriques examined it more closely as an ester. He found a greatly increased saponification number, which, in this case, could not be ascribed to a splitting up of the molecules, as the saponification lye from which the oxyacids separated showed no increased acid value. He regarded the results as speaking more of oxyabietic acid than lactonic acids. Now Henriques has himself shown that unsaturated alcohols, like geraniol and linalol, behave to alcoholic potash in a much more stable manner than aromatic alcohols, like cinnamic alcohol. The analogous conclusion arrived at is, that the fatty acids, oxylinoleic and oxylinolenic, behave like the aromatic oxyabietic acids, and that the high saponification value is due to the unsplit-off molecules of weak acid groups.

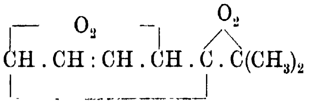
In the year 1900, C. Engler published his autoxidation theory, which he afterwards elaborated with J. Weisberg. It consists in the action of atmospheric oxygen on the unsaturated compounds, not of oxygen atoms but of oxygen molecules and the double-linked carbon atom. It includes primary peroxides which have the property of parting with half of the absorbed oxygen to another oxidisable body acceptor. Under certain circumstances the unsaturated body, the autoxidator itself, may act as acceptor functioning molecularly, later from the primary formed peroxide. When no acceptor is present then the peroxide uses its active oxygen for an inner oxidation by fixing up a molecule. Instead of such absorption, polymerisation may occur. It follows, therefore, that autoxidation as well as polymerisation may occur simultaneously, viz. in the treatment of the unsaturated free valencies, in the first instance by molecular oxygen, in the last instance by the free valencies of each molecule. In both cases the unsaturated nature of the body is at an end. As far as specially concerned the unsaturated fatty acids and their esters, Engler and Weisberg used Weger's calculations as proof, and gave a series of examples under the heading of direct autoxidation. They state that linseed oil on autoxidation does not act as self-acceptor but absorbs molecular oxygen exclusively. Hence on the other hand, on slightly heating strongly unsaturated fatty acids their behaviour towards atmospheric oxygen is demonstrated. So it is possible to bring forward here as example the unsaturated hydrocarbide dimethylfulven



$$\mathrm{CH:CH.CH:CH.C:C(CH_3)_2}$$

which like linoleic acid contains three double bonds. It was dissolved in benzol solution and shaken with air or oxygen for 4 to 6 days by which it separated a white amorphous precipitate. Light and increase of temperature hastened the separation. The analysis showed a diperoxide, $C_8H_{10}O_4$. The body had explosive properties.

It is insoluble in benzol petroleum ether, ether and alcohol. It dissolves on heating in nitrobenzol and glacial acetic acid with chemical absorption. In aqueous alkali it dissolves readily in the cold, but under decomposition. The diperoxide is very unstable, its explosive properties are in evidence even under the influence of light and still more rapidly on heating. It melts between 120° C. and 130° C., becomes soluble in alcohol and cold acetic acid, etc. If a boiling benzol solution of dimethylfulven be treated with oxygen the above peroxide does not remain as chief product but only secondary, soluble and non-explosive bodies. If the benzol solution be shaken with a solution of sodium sulphindigotate of known strength, the latter will require 50 per cent. of its weight oxygen, which will be taken from the dimethylfulven. The diperoxide, $C_8H_{10}O_4$, is thus reduced *in statu nascendi* to a body $C_8H_{10}O_2$. As to the constitution of these bodies, Engler and Falkenstein believe the diperoxide to have probably the following formula :—



$$\underline{\overline{\mathrm{CH} . \mathrm{CH} : \mathrm{CH} . \mathrm{CH}}^{\,O_2} . \overset{O_2}{\mathrm{C}}} . \mathrm{C}(\mathrm{CH_3})_2$$

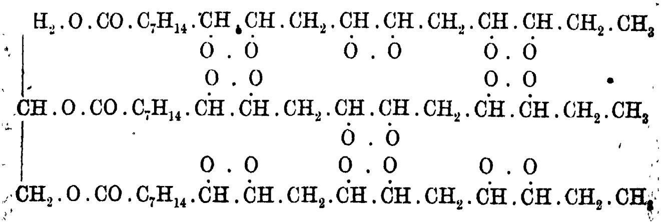
so that on autoxidation one of the three double bonds remains.

Lactones.—Lewkowitsch believes the increased saponification number of linseed oil on oxidation is due to the formation of lactones. He tried to prepare these from the oxyacids by neutralisation with aqueous lye, and agitated the solution with ether. This left a viscous fluid, insoluble in alcohol, with the saponification number 35·5, but the decomposition of the saponified lye yielded a body with the acid number 57·4. Finally, the oxyacids containing the lactones gave a higher saponification number than acid number. Lewkowitsch concludes therefrom the fresh formation of lactones, but Fahrion believes Henriques' lactonic acids nearer the mark. Lewkowitsch then strongly asserts that the oxyacids are considerably more soluble in water than the petroleum ether acids. The latter give a slight ester and acetyl number, in which the presence of a small quantity of lactones and hydroxyacids occurs. On the other hand, the probability is undoubted that the fatty acids from petroleum ether dissolve a certain quantity of oxyacids.

Autoxidation.—In 1904 Fahrion tried to bring Engler's autoxidation theory into harmony with the known process of oil drying. That linseed oil, chiefly as primary autoxidation product, liberates peroxide can be established qualitatively. It was often shaken with water for 8 days and left in the open air, then a drop of dilute sulphuric acid added, filtered, and to the filtrate potassium iodide and starch added. A decided blue coloration was produced, whilst a blank test remained colourless. When the above experiment was repeated, after a week, but instead of with ordinary linseed oil, with blown oil or dried linseed oil, t following coloration occurred with titanium sulphide, viz. a yellow oration. The autoxidation products are very difficultly soluble, in d water. It was finally shown that Mulder's combustion figures linoxin correspond with a mixture of hexa-oxylinolenic acid and a-oxylinoleic tri-glyceride.

	C.	H.	O.
Calculated for $C_3H_5(C_{18}H_{30}O_8)_3$ . .	51·0	7·9	33·1
„ „ $C_3H_5(C_{16}H_{32}O_6)_3$ . .	63·9	9·2	26·9
Mulder found	62·5	8·9	28·6

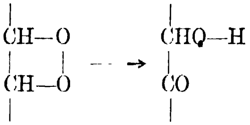
Linoxin is thus a mixture, in varying proportions, of above glycer- . Its formation was firmly ascribed to the splitting off of water, finally it yields, on saponification, acids soluble in petroleum ether, nd these, along with the petroleum ether insoluble oxyacids, give onsiderable iodine numbers, in which hexaoxylinolenic and tetraoxy- inolic acid absorb no more iodine. Linseed oil consists of mixed lycerides, and the oleic acid and the solid fatty acids are mixed up n the drying process, and are therefore present in the linoxin. The eroxide does not resist excess of alkali, without chemical change, so he oxyacids are no longer to be regarded as the product of a molecular ixation of the original primary peroxide. The great variation in their oxygen content is partially explained by successive oxidation, partly by splitting off of water. Under this point of weight, Fahrion claims hat his combustion results are not in favour of Engler's theory, but of he lowest oxidised bodies, but at no time lower than that one molecule of oxygen has been absorbed. A polymerisation of the original prim- ry peroxide would seem very probable, as with acetone peroxide in wo instances. It is presumed, however, that in special cases a eutralisation of the double bonds, or a concatenation of the oxygen toms, into a higher molecular weight is possible. This will be more eadily understood with the formula of hexaoxylinolenic acid before he eyes:—



$$\begin{array}{l}
H_2.O.CO.C_7H_{14}.CH.CH.CH_2.CH.CH.CH_2.CH.CH.CH_2.CH_3\\
\qquad\qquad\qquad\qquad O\;.\;O \qquad\quad O\;.\;O \qquad\quad O\;.\;O\\
\qquad\qquad\qquad\qquad O\;.\;O \qquad\qquad\qquad\qquad O\;.\;O\\
CH.O.CO.C_7H_{14}.CH.CH.CH_2.CH.CH.CH_2.CH.CH.CH_2.CH_3\\
\qquad\qquad\qquad\qquad\qquad\qquad\quad O\;.\;O\\
\qquad\qquad\qquad\qquad O\;.\;O \qquad\quad O\;.\;O \qquad\quad O\;.\;O\\
CH_2.O.CO.C_7H_{14}.CH.CH.CH_2.CH.CH.CH_2.CH.CH.CH_2.CH_3
\end{array}$$

Autoxidation Peroxides.—Blown linseed oil contains the free acid as a yellow syrup soluble in petroleum ether. On saponification it is insoluble up to one-half in petroleum ether, from which it appears that the original primary peroxide of linolenic and linoleic acid is soluble in petroleum ether, and that the fixation product thereof is insoluble. Genthe also takes it that the primary peroxides remain. Trials to isolate them were unsuccessful. However, he has shown incontestably that autoxidation goes hand in hand with the increase in the molecular weight. He heated linseed oil in a small beaker glass, covered by a lid of sheet aluminium, on which a glass cylinder for storing air was fitted, for 300 hours at 135° C. Samples were taken daily and the molecular weight taken, with ether as solvent. It rose in that time from about 800 to 1400. The oxidised oil was a red-brown, completely transparent, rubber-like mass. There is strong reason to believe that no polymerisation occurred during the above research, the molecular weight did not at any time double, and the phenomena can be attributed exclusively to condensation. Finally, Genthe recognised second reaction in the drying process, consisting in a slow combustion of the organic substance. A short notice of Fahrion's research on the autoxidation of rosin may find a place here. The autoxidation product gave peroxide reaction and was insoluble in petroleum ether. Its composition was a mixture of di-and tetraoxyabietic acid, $C_{20}H_{30}O_4$ and $C_{20}H_{30}O_6$. On heating above 100° and treating with alcoholic sulphuric acid, which is known not to etherify the COOH group, petroleum soluble derivatives were produced, with only slight agitation of the soda solution with ether of diminished acidity.

Later Fahrion isolated the original primary peroxide. The research was mainly on linoleic acid, using cotton-wool as dividing material. The product was first shaken with petroleum ether to remove the unoxidised portion. Then the autoxidised product taken up with ether left it as evaporation residue in the form of a thick syrup. It contains a considerable amount of active oxygen which it readily cedes to KI in acetic acid solution. At the same time the product exhibited all the properties which Mulder ascribed to linoxin. Above all things it passes on heating, and by the action of alkalies, into red linoxic acid, changing the active oxygen content, apparently owing to the fixing of this peroxide on a ketoxic group:—



$$\begin{array}{l} | \\ \mathrm{CH-O} \\ |\quad\ \ | \\ \mathrm{CH-O} \\ | \end{array} \dashrightarrow \begin{array}{l} | \\ \mathrm{CHO-H} \\ | \\ \mathrm{CO} \\ | \end{array}$$

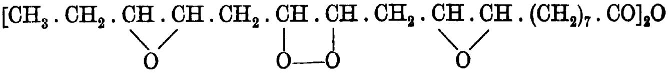
This change can proceed without any change in colour, e.g. prolonged heating of white linoxic acid with dilute HCl; finally it is produced on storing it a long time by itself. Therefore, red and white linoxic acid are distinct from each other, since the last consists exclusively of ketoxic acids, whereas the latter contains active oxygen as peroxyacids. Mulder was, therefore, correct when he looked upon (a) white and (b) red linoxic acids as differing chemically. But

Bauer and Hazura were also correct when they described the red coloured acid as an unknown decomposition product. The production of potassium linoleate during oxidation, in neutral solution, points also to a ketoxy group. Similar products are formed during the fixation of white linoxic acid. Again Holde and Marcusson obtained ketoxystearic acid, $C_{17}H_{32}O(OH)COOH$. The petroleum ether portion of the autoxydation products contains active oxygen; finally, during saponification it becomes partially insoluble in petroleum ether. White linoxic acid becomes during saponification partially soluble in petroleum ether. These results are explained by the etherification of fatty and oxyacids. If linoxic acid be dissolved in soda solution, and this solution shaken with ether, the latter leaves a yellow syrup with the molecular weight 600. Its formation requires 2 molecules and is explained by the following equation:—

$$2R(OH)(COOH) = H_2O + ROH . CO . O . R . COOH.$$

Thus the perfectly neutral anhydro-derivative may remain as shown by the behaviour of linoxic acid, and when heated above 100° C., it becomes partly insoluble in soda and ammonia. By saponification, the insoluble part becomes soluble in above solution. However, Mulder's analyses of linoxin, with a saturation of the double bond by oxygen, still holds good. But a series of Mulder's and Fahrion's oxyacid analyses with the other data regarding linolenic acid and linoleic acid, show that a double bond always remains intact as in dimethylfulven. Autoxidation of linseed oil is not so uniform as that of linolenic acid. It leaves as chief product a still soluble yellow syrup with considerable active oxygen content.

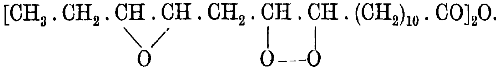
Dried Linseed Oil—Linoxin.—Finally it yields the penultimate product of the autoxidation, insoluble in all solvents, linoxin. On saponification, linoxin gives a certain amount of solid fat, a proof, therefore, that it exists at least partly as glyceride in the form of mixed glycerides from the linseed oil, and, therefore, taking part in the drying process. Orloff found for a complete dry linseed oil residue an iodine number 14·1. It set no iodine free from an acidulated KI solution, yet it liberated active oxygen from an alkaline potassio-mercuric iodine solution, from which an equivalent quantity of metallic mercury was liberated. In ether the dried oil was only partially soluble. To the soluble portion in virtue of his analyses, Orloff ascribes the following formula:—



$$[CH_3 . CH_2 . \underbrace{CH . CH}_{O} . CH_2 . \underbrace{CH . CH}_{O—O} . CH_2 . \underbrace{CH . CH}_{O} . (CH_2)_7 . CO]_2O$$

Orloff's formula for dried linseed oil, soluble portion.

On the other hand, to the ether insoluble portion, also likewise from the linoxin, the following formula was given:—



$$[CH_3 . CH_2 . \underbrace{CH . CH}_{O} . CH_2 . \underbrace{CH . CH}_{O-O} . (CH_2)_{10} . CO]_2O.$$

Orloff's formula for dried linseed oil, insoluble portion.

These formulæ contain a series of errors. In the first place, the ether soluble portion is more highly oxidised than the ether insoluble, the first was a derivative of linolenic, the second of linoleic acid, but their formula is comparable one with the other. Further, molecular as well as atomic oxygen was absorbed, and finally, dried linseed oil still contains glycerine. Besides, all these errors are capped by the fact that "linoxin" is a mixture of several bodies, and therefore the establishment of any such formulæ is quite impermissible.

The chemistry of autoxidation during blowing of linseed oil must be much the same as during drying, only it is to be remarked that the primary peroxide at high temperatures is fixed, and that the splitting off of water is greater. Fahrion found in an oil blown at 150° C. 0·4 per cent. of active oxygen, whilst Mulder over six years' standing found peroxide building and consequent oxidation. Owing to the intensity of the reaction during blowing, a series of volatile bodies are given off, hence are not present on drying. H. Nordlinger isolated acids of boiling-point 190° C. and over, alcohol aldehydes and esters of boiling-point 150° C. and higher. Looking to data hitherto available, and its confusing nature, it must be acknowledged that the process of autoxidation from its chemical aspect is in nowise completely clear. In several ways much light is thrown by the following:—

1. It is certain that the primary peroxide remains, and seemingly persistently, so that exclusively molecular oxygen is absorbed and also that the primary peroxide does not even by its active oxygen lend itself to linseed oil as a self-acceptor. It is difficult to believe that, first the linolenic, then the linoleic acid absorb oxygen, leaving the saturated fatty acids untouched. As regards oleic acid it does not resist the action of the air. Its change must, as Mulder suggested, lie more in the direction of the rancidity of the oil, with lowering of the iodine numbers. In any case, at the ordinary temperature oleic acid leaves no oxyacids insoluble in petroleum ether, and it can be taken as certain that it in nowise shares in the drying process. However, it can occur in the form of mixed glycerides in the ethereal solution of linoxin, along with the unsaturated fatty acids, which also contain linolenic or linolic acids. Likewise, oleic acid can lower their iodine numbers by secondary processes, which have nothing in common with the real drying process. It is taken that linseed oil contains 18 per cent. of oleic acid, therefore the iodine number of 14 for dried linseed oil. On the other hand, Orloff's value of 14 cannot be ascribed to oleic acid alone; then the oxyacids separated by

saponification, which contain oleic acid in traces, still absorb iodine. This is due to one of the double bonds of linolenic and linolic acids remaining intact during autoxidation, which clears the matter up greatly. This opinion is favoured by the high oxygen content of different oxylinolic and oxylinolenic acids.

2. It is certain that during the oxidation of the linseed oil part of the glycerine is split off. Both Mulder and Bauer and Hazura assumed that this splitting off was due to the progress of oxidation. Mulder showed that under the term free fatty acids, both oleic acid and saturated fatty acids occurred. Bauer and Hazura make the same assumption; they go farther and imagine that only solid fatty acids and free oleic acid occurred free, and that of linolic and linolenic acids no trace occurred. As to the latter assumption, there is no proof; facts are against it. As to spontaneous fat splitting in a partially split fat, the free fatty acids have abundant glycerine in their composition, so that under the term free fatty acids contained in linseed oil both linolenic and linolic acids are included.

3. It must not be forgotten that in several processes during the heating of linseed oil with simultaneous blowing, the thickening so produced is due to a greater or less extent to autoxidation. That it is due to polymerisation is improbable. Different reasons point to condensation. During the fixing of the primary peroxide OH groups are formed, such are free COOH groups which are also produced. For this reason the molecular weight rises from 800 to 1400, as determined by Genthe, therefore no polymerisation can intervene where condensation occurs. Moreover, in condensation processes the iodine number does not lower, but rises. Hence by air blowing, thick boiled oil shows a great lowering of the original iodine number, and during drying great lowering occurs, which is only to be partially ascribed to autoxidation.

Self-autoxidation of the Autoxidiser in Addition to Autoxidation of Acceptor.—The autoxidiser oxidises itself as well as the acceptor by producing a stable compound, which can no longer serve to produce a peroxide; to continue the autoxidation a fresh quantity of autoxidiser is required which necessitates a definite relation between the two substances. That is why linseed oil may still dry satisfactorily if non-drying oils or other non-drying bodies, e.g. greasy lamp-black, are added to it, but only within certain limits compatible with the conditions just enunciated. Finally, certain metallic salts, capable of forming oxides of different degrees of oxidation, impart great drying properties to linseed oil, when placed in suitable contact therewith. Lead, manganese, and cobalt manifest these properties in a specially energetic manner. Added (1) as compounds soluble in oil (rosinates, linoleates), or (2) placed in contact with oil in the form of oxides they endow it with an aptitude for oxidation altogether remarkable. In the first case (1) they play the rôle of autoxidisers, in the second instance (2) there is partial saponification of a part of the oil with the formation of a manganous or plumbic salt of the fatty acids of the oil, which dissolves therein and which afterwards plays the rôle of autoxidisers, as in the previous instance.

Manganese Compounds and their Action.—Traces of a manganese salt added to a mixture of (*a*) oxidisable bodies with (*b*) oxidising bodies, start or accelerate very appreciably the oxidation reaction. The manganese compound, besides its action as an autoxidiser on oil, favours the formation of organic peroxides and accelerates the oxidation produced by the latter. For that purpose only an infinitesimal quantity is required (see table), and the oil so treated may be considered as practically exempt from mineral compounds. It does not become brown in the air only; the nature of the acid forming the manganese salt has a great effect on the intensity of the reaction.

Summary of the Autoxidation Bertrand Theory.—1. The drying of linseed oil is produced by the conversion in contact with air of several unsaturated liquid glycerides, with several double bonds or links into peroxides, which completely oxidise the oil. This reaction is very slow.

2. By adding spirits of turpentine to the oil the action is accelerated, for this essential oil readily produces in the air a peroxide which completely and rapidly oxidises the mixture.

3. Finally, the addition of a manganese salt still further accelerates the rapidity and increases the energy of the reaction:—

(*a*) By acting as a mineral ferment (see Barruel and Jean) when used in mere traces, in presence of a substance which can readily convert itself into an organic peroxide such as spirits of turpentine.

(*b*) By acting directly on the oil as an autoxidiser when it is used in higher proportion, and in this case it shares this property with lead salts.

The process when an autoxidiser of this nature is used may be written thus:—

A. Autoxidiser.

B. Acceptor.

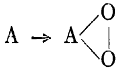
Here the autoxidiser does not participate in the final oxidation, it cedes all the oxygen which it has fixed and recommences acting as a carrier between the atmospheric oxygen and the acceptor. It is unnecessary to have a great quantity in use, a minimum quantity suffices.

As far back as 1883 Livache is credited with having shown that manganese is a more active drier than lead, but that was proved long before the eighties. Vincent pointed it out before 1870, and Faraday long before him. It was even proved by Vincent on 2 ton batches of oil as far back as 1870, and Vincent acknowledges that the idea of using manganese came from Faraday. In a word, the use of manganese goes back beyond the memory of any man now living, and Germany had nothing to do with suggesting its use or of cobalt.

Mineral Ferments.—The important rôle which manganese salts play in a whole host of oxidations, both natural and artificial, has been shown by Bertrand. They coexist in the oxidising ferments from which fact they are termed mineral ferments.

$$A + O_2 \rightarrow AO_2$$
$$AO_2 + B \rightarrow A + BO_2.$$

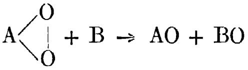
A. Autoxidiser



$$A \rightarrow A\left\langle\begin{matrix}O\\|\\O\end{matrix}\right.$$

conversion into peroxide.

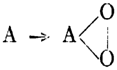
B. Acceptor



$$A\left\langle\begin{matrix}O\\|\\O\end{matrix}\right. + B \rightarrow AO + BO$$

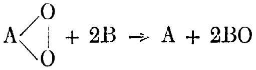
oxidation properly so called.

A. Autoxidiser



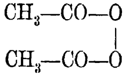
$$A \rightarrow A\left\langle\begin{matrix}O\\|\\O\end{matrix}\right.$$

B. Acceptor



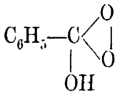
$$A\left\langle\begin{matrix}O\\|\\O\end{matrix}\right. + 2B \rightarrow A + 2BO$$

Haller has since pointed out the presence of stearic acid and a little arachidic acid. However that may be, we may take linseed oil to consist of glycerides of different fatty acids (1) saturated fatty acids $C_{14}H_{28}O_2$, myristic acid $C_{14}H_{28}O_2$, stearic acid $C_{18}H_{36}O_2$, and palmitic acid $C_{16}H_{32}O_2$; (2) the unsaturated fatty acids to which belong all the others. The latter class is differentiated from the former as they comprise double links in their chain: $CH = CH$ corresponding to unsaturated carbon atoms. These double bonds are more or less numerous; oleic acid only contains one, linoleic acid two, linolenic acid and isolinolenic acid three. Oleic acid is also present in other and non-drying oils; it is not characteristic of the drying property of linseed oil, which is undoubtedly due to the presence of linoleic, linolenic, and isolinolenic acid peculiar to that oil, that is to say, to fatty acids containing two or three double bonds corresponding to four or six atoms of unsaturated carbon atoms, have unsatisfied valencies and consequently capable of fixing other atoms. The drying of linseed oil is due to the absorption of oxygen, and as in this reaction the weight increases, the oxygen absorbed is not utilised for a partial combustion of the product, but is fixed by addition. It is therefore quite rational to assume that this oxygen has saturated the double links. This is shown by the chemical examination of linoxin; it shows that this product no longer contains double bonds. That linseed oil agitated with air dries more rapidly has already been seen, also when it is mixed with turps or with the mineral bodies termed driers, and the effect is appreciably greater when these three conditions are combined. As regards turps the fact is explained by the fact that in contact with this liquid, atmospheric oxygen becomes more active. It is well known that an aqueous solution of indigo carmine is bleached in the air when little turps is added to it. The oxygen of the air which does not act on this colour, destroys it under these conditions. Although it has been asserted that ozone is formed in contact with turps, it is not a transformation of that which causes it, for if in the previous experiment the oxygen of the air used be measured it will be found that the volume of oxygen absorbed is double that required to decolorise indigo. Oxygen is therefore also fixed by the turps, and it is to the compound so formed that the bleaching is due. If we go back to the mixture of turps and linseed oil the same reasoning applies—the turps cause the oxidation of the oil by absorbing oxygen. These oxidation phenomena due to turps have been studied more especially by Bach, Engler, and F. Weisberg, who have shown that under these conditions turps, or more exactly, pinene, a non-saturated hydrocarbide of which turps consists almost entirely, is converted by contact with the air into a peroxide by the absorption of two atoms of oxygen which is fixed by the double link; the compound formed R—O—O—R is very unstable and behaves like hydrogen peroxide H—O—O—H by abandoning an atom of oxygen to the oxidisable body termed, an acceptor being itself converted into a more stable body R—O—R or H—O—H. This property of forming peroxides is shared by a large number of organic bodies; amylene, trimethyl ethylene, hexylene, unsaturated hydrocarbides form peroxides. Certain aldehydic bodies possess the same properties. Acetyl peroxide and benzaldehyde peroxide are well known—



$$\begin{array}{r} CH_3{-}CO{-}O \\ | \\ CH_3{-}CO{-}O \end{array}$$

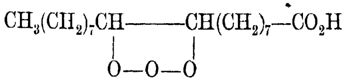
Acetyl peroxide.



Benzaldehyde peroxide.
Perbenzoic acid.

The non-saturated fatty acids may themselves yield peroxides.

If they do not possess one double bond, for example in the case of oleic acid, the peroxide is not formed in contact with air, the oil does not dry, but none the less this fatty acid can yield a superoxygenated compound when treated by ozone, as shown by Molinari and Soncini as well as Harries and Thieme. The ozonide of oleic acid possesses the constitution :—



$$\begin{array}{l} CH_3(CH_2)_7CH{-}{-}{-}{-}CH(CH_2)_7{-}CO_2H \\ \qquad\qquad\quad | \qquad\quad | \\ \qquad\qquad\quad O{-}O{-}O \end{array}$$

The unsaturated fatty acids possessing several double bonds form peroxides in contact with air. These peroxides then act on the oil itself which plays the rôle of acceptor, and the drying of the oil thus proceeds quite rapidly as soon as an appreciable quantity of peroxide is formed. If non-drying oils be added to linseed oil they likewise dry in spite of their non-drying properties, oxidation occurs by entrainment, the non-drying oils play the part of acceptors and are oxidised after the manner of indigo carmine in contact with turps and air. That explains how linseed, which contains a considerable proportion of saturated fatty acids, dries right to the core although the same fatty acids do not dry alone. During the process of oxidation all the organic bodies added to paint participate in the oxidation. It is well known that canvas which has been painted on directly is "burnt" by the painting, and that the painting is always insulated from the canvas by a special coating. The pigments themselves (see Vol. III.) do not escape this action and are subjected to energetic oxidation when used ground in oil. It is thus necessary that they should be as little sensitive to this action as possible, and more particularly that they should be completely insoluble in oil and turps besides water.

Permanent pigments should not only resist sunlight but also the oxidising action manifested as the paint dries. An example will suffice to show the special attention which should be brought to bear upon the point. Indigo, a natural organic colour, is much used in dyeing owing to its very great resistance to the oxidising action of sunlight. It should therefore constitute in oil-painting a very strong colour. Yet what do we find if we heat indigo with linseed oil to 90°? We get rapid solution, cold, it shows a dark green tint. The filtered solution exposed to the air is rapidly decolorised. The indigo has been destroyed amidst a mass containing organic peroxides. As all organic colours are oxidisable they must be rendered completely insoluble in oil by converting them into lakes, analogous to madder lake. In a general way the bodies, the above-named substances called by Engler and Wöhler autoxidisers, oxidise the bodies with which they are mixed acceptors by becoming converted into peroxides which cede to the latter one of the two molecules of oxygen absorbed reserving the other. For the oxidation of a given weight of substance (acceptor) it is necessary to use an equivalent quantity of autoxidiser.

Luminous rays act very favourably on the formation of peroxides, that is why linseed oil dries more rapidly in sunlight. Its drying capacity is increased. If we compare the effect of the different rays which accompany or compose sunlight, it is found that the rays with a short wave length, the ultra-violet rays, have an extremely intense action. Linseed oil submitted to these rays dries very energetically. Let it be well understood that it is possible to add directly, organic peroxides, which may be prepared by chemical means, and rapid drying oils may be so obtained which do not contain a trace of mineral matter.

Comparative Rapidity of Drying in Dry Air and in Moist Air.—The question whether manganese boiled oil dried best in dry or moist air was examined by Lippert. His results, if curious, are interesting. A boiled oil rich in manganese dries faster in dry air. Hence the amount of water in the air, and that of manganese in the boiled oil, act in diametrically opposite directions. Weger asserted that, generally, lead boiled oil dried fastest in damp air, manganese boiled oil in dry air, and he certainly got very different results with manganese borate boiled oil, which is comparatively poor in manganese. He mentions a manganese borate boiled oil that dried in 6 hours in cold damp weather, and took 12 hours to dry in a warm atmosphere. Lippert first compared the drying of the boiled oils in a current of perfectly dry air, which had been freed from any trace of aqueous vapour by passing through sulphuric and phosphoric anhydride, with that of boiled oils in an ordinary room, in which the dampness of the air was regularly tested by a hygrometer, but he found these tests could be dispensed with.

Choice of Drier—Manganese Driers.—It has been shown that the best results are obtained by the use of lead and manganese. An oil boiled in contact with manganese driers dries quicker than one boiled with lead driers. When boiled oil is free from lead it has the advantage of not being altered by sulphur compounds. The receipts given for the different driers to be added recommend the use of the borate and the hydrated oxide of manganese to the exclusion of all lead compounds, and the boiling may be done as suggested. The superiority of oils having manganese as their only drier is so decisive that attempts have been made to manufacture such oils directly.

1. *Borate of Manganese.*—Two pounds of very white borate of manganese, free from iron and finely ground, are added with constant stirring to 1 gallon of oil heated to 100° C. (212° F.). When complete incorporation is effected the heat is raised to 200° C. (392° F.). One hundred gallons of oil are heated in a pan until bubbles of gas commence to come off, when the preceding mixture is added in a thin stream. The heat is raised to about 200° to 220° C. (392° to 428° F.), and after 20 minutes' boiling an oil is obtained which rapidly dries to a bright elastic coat. It is absolutely necessary only to use borate of manganese completely free from iron. It may be prepared by adding a solution of borax to a solution of manganese chloride, so long as a precipitate forms which is washed with water and dried. A perceptibly white product is thus obtained. As manganese ores are liable to contain iron, lime, and other impurities this method of preparing borate of manganese is apt to give an impure product; a better method is that given. The drying properties of this salt are such that it is claimed by some that it can transform linseed oil into a quick-drying oil at a temperature as low as 40° C. (104° F.), e.g. if in a flask containing linseed oil we suspend a small linen bag containing borate of manganese (3 oz. of borate to 100 oz. of oil), and if we place the flask in a warm place we obtain in 15 days a quick-drying oil. But all these trivial processes are misleading. Life is

too short to wait 15 days for oil to dry no quicker than boiled oil, and only under exceptional conditions, such as the presence of free fatty acid in the oil and free hydrated oxide of manganese in the borate, can the oil be acted on at such low temperatures. Commonsense might tell those who make such extravagant claims for borate of manganese that in the cold it is almost inert. A better oil is said to result if, instead of employing borate of manganese alone, we employ a mixture of borate of manganese and oxide of lead, which is practically the same, because the reaction which ensues introduces oxide of manganese, but the latter may be added directly in the form of the hydrated oxide—a dense, brown product; finally, it can be introduced by utilising reactions similar to the following:—

2. *Hydrated Oxide of Manganese and Air.*—One thousand pounds of oil are heated to 70° to 80° C. (158° to 176° F.). 3 lb. of crystallised manganese sulphate are dissolved in a very small quantity of water by the aid of heat; 10 lb. of caustic potash dissolved in a small quantity of water are added; the whole well stirred and run into the oil. The mass turns brown, and brightens at the same time. An india-rubber tube, to the end of which a rose nozzle is fixed, is introduced into the pan, and by means of a pump air is injected for 4 or 5 hours until the brown coloration has disappeared. The oil to which the above mixture has been added falls in drops inside a pipe, where a current of air circulates the reverse way. The oil is again elevated, and made to fall again, and so on until the brown coloration disappears. It has been further proposed to use the natural black oxide of manganese—pyrolusite.

3. *Black Oxide of Manganese and Sulphuric Acid.*—A mixture of 2 lb. of finely ground pyrolusite and 2½ lb. of sulphuric acid is added to 100 lb. of linseed oil heated between 180° and 200° C. (356° to 392° F.). After about an hour, a milk of lime, obtained by slaking 1 lb. of quicklime, is added, the whole well stirred, and filtered through canvas.

4. *Various Processes.* (*a*) *Treating Litharge Boiled Oil with Borate or Sulphate of Manganese.*—Livache claims that a very quick-drying oil—free from lead—whose drier is manganese may be obtained in a roundabout way by slightly heating or simply agitating an oil which has been boiled with litharge, with borate or sulphate of manganese. The oxide of manganese, he says, replaces the oxide of lead, which is precipitated in the state of insoluble lead borate or lead sulphate.

(*b*) *Boiling Linseed Oil with 5 per Cent. Lead Oleate.*—One hundred gallons of linseed oil are heated with 50 lb. of lead oleate. But as oleic acid is not a suitable acid with which to combine a drier; the oleate of lead has for a long time been replaced by manganese linoleate and also by manganese rosinates which are used in smaller proportion. Neither of these exert a counter influence on drying like oleic acid.

Zinc Driers.—Linseed oil is sometimes boiled after the addition of white lead, lead acetate, and dehydrated zinc sulphate. The function of zinc sulphate in oil-boiling and varnish-making is obscure; it is added with the idea of imparting elasticity, also to remove water. Again, attempts have been made to substitute lead salts by pure oxide of zinc, but after boiling the resultant oil dries slowly, and the oil so prepared has no advantage over a litharge-boiled oil, except that it is not blackened to counteract this irremediable drawback by sulphuretted hydrogen. Livache precipitated the lead of a litharge-boiled oil by means of a suitable manganese salt, such as the sulphate, but that is a very roundabout way of introducing manganese into the oil, and seems so unnecessary, too, as both manganese linoleate and manganese rosinate, to say nothing of the acetate or even the borate, dissolve very freely in hot linseed oil. But it is more than probable that the precipitation of the lead dissolved in the oil is anything but complete, and that the good results claimed by Livache from this style of working were due to the conjoint action of lead and manganese. Oxide of zinc has been added to the salts of manganese employed in oil boiling, but if the zinc oxide did any good it was due to the liberation of manganese oxide. Leaving out of account the advantage—often very appreciable—of obtaining an oil which does not blacken in contact with sulphuretted hydrogen, it would appear that the oil does not dry quite so quickly, nor so uniformly and well, as when a manganese salt is added in presence of lead oxide. It has been recommended not to heat the oil with driers beyond 120° to 127° C. (248° to 260·6° F.), but to project into the oil after several hours' boiling $\frac{1}{400}$th of its weight of water, mixed with $\frac{1}{50}$th of its weight of litharge, in the form of fine drops. But this dangerous process, due to Bartky and tried in Germany, appears to be but little used, if at all.

Barruel and Jean found that an oil which did not contain any thickened oil, nor drier, begins on exposure to give off carbonic acid, but that, under opposing circumstances, carbonic acid is disengaged after 8 to 10 hours contact. Another important point which follows from their experiments is that for the intestinal movement to manifest itself, the temperature must be brought to + 15° C. whilst below that temperature down to 6° C., the action of accelerating or exciting agents is always weaker. The necessity for a medium temperature points to an analogy between this phenomenon and that of fermentation. The increase in weight of a coating, after complete drying on tin, rose to 16 per cent. of the weight of the oil used. They also discovered that the direct or reflected light of the sun exercises a manifest influence on the phenomena of the drying of oils. Thus a sq. metre on which a coat of paint made from manganese-treated oil and zinc white had been applied, and left in a dark place, only increased 1·1 grammes in 7 hours, and 2·23 in 20 hours, whilst the same surface left in the laboratory at the same temperature, but exposed to the light from a cloudless sky increased 3·3 grammes in 7 hours, and 4·42 grammes in 21 hours. Under the influence of the solar rays, absorption is still more rapid than in the preceding case. In an experiment lasting 4 hours, a surface 1 metre square, which had been coated with white paint and drier, had increased 4 grammes in weight and disengaged 435 milligrammes of water and 1 gramme of carbonic acid. The water would appear to originate in the large surface of the glass vessels, used in the experiments, for in the different weighings it was not proportional to the carbonic acid disengaged. The above chemists contended that the absorption of oxygen by drying oils, under the influence of heat and light, is the result of an internal movement, which operates similarly to fermentation. Barruel and Jean's views appeared to be supported by numerous facts. They found bodies which added in infinitely small quantities under the influence of the solar light and a moderate temperature, cause drying oils to dry in a very short time, or to speak more plainly resinify them, with the result that carbonic acid is disengaged, whilst the oxygen is fixed by the oil. Barruel and Jean assert that there is an oleaginous as well as a lactic acid fermentation. In oil boiling, the oxides absorbed by the oil are imperfectly reduced which gives rise to the formation of carbonic acid. The reduced oxide is thus converted into a body, which operates on the oil after the fashion of a ferment, and the proof of it lies in the fact that boiled oil possesses no drying properties unless it contain dissolved oxide. Barruel and Jean found that the substances which possess this property in the highest degree are for the most part metals of Thenard's third class, manganese, zinc, iron, cadmium, and amongst that group it is the protoxides of cobalt and of manganese that have given the most satisfactory results. In some cases protoxide of iron is said to behave in the same way but with less energy. Barruel and Jean, so as to find a ferment, or an innocent drier working energetically on drying oils, tested compounds of the above oxide which, leaving to these oxides all their exciting force, would be easily made on the large scale. But such is not the case with the above protoxides which are difficult to prepare, and cannot be preserved in contact with air. They first tried the organic and inorganic compounds of the protoxides of cobalt and manganese. They afterwards found that carbonic, phosphoric, sulphuric, and hydrochloric acid as well as the greater number of vegetable acids, retain the above oxides too energetically and almost entirely annul their effects. The salts of these oxides in the basic state have, it is true, a more marked action, but of all inorganic acids it is boric acid in combination with the protoxides of cobalt and manganese which gave the best results. The ratio according to which the borate of the protoxide of manganese may start the fermentation of drying oils is 1 to 1½ parts by weight in 1000 parts by weight of the oil, that is 0·001 per cent. Barruel and Jean remarked that the borate of manganese which they used and tested was not an anhydrous salt, but contained about 25 per cent. of water and appeared to act in this way: a portion of the protoxide is eliminated by the effect of light and heat, it absorbs oxygen from the air to be converted into peroxide, and very soon the oil begins to set and the coating at this moment begins to colour slightly, but this coloration disappears when the coating is dry. If 1 to 2 per cent. of borate be used, calculated on the weight of the oil, the brown coloration of the coating persists. Two organic acids yield with the protoxides of cobalt and manganese salts analogous to those yielded by boric acid, viz.: benzoic acid and hippuric acid. Resins behave like acids but to a less extent. The use of hippuric acid seems to Barruel and Jean to be advantageous, as it would utilise a neglected product of the farm.

Lead and Manganese Salts as Driers.—Besides the *oxides* of lead and manganese we may employ certain *salts* of these oxides as driers. But their choice would appear to be subordinate to their degree of solubility in the oil, and to the way they behave when heated along with the oil. Further, all the numerous salts proposed have been discarded except the acetate (sugar) of lead and borate of manganese, and the reason is not far to seek. These salts decompose when heated, and yield as a final result either the oxide of lead or finely divided metallic lead, or oxide of manganese, of which the valuable function is well known.

1. *Acetate of Lead.*—This salt melts in its water of crystallisation at about 75° C. Above 100° C. it loses water and a little acid, yielding the sesquibasic acetate, which towards 280° C. is completely decomposed, giving off carbonic acid and acetone and leaving as a residue metallic lead in an extremely fine state of division (spongy lead). We have seen the important rôle this plays in stimulating the drying properties of oil.

2. *Borate of Manganese.*—Again, on the other hand, we have in borate of manganese a very unstable salt, as is the case with borates in general. The affinity of boracic acid for oxide of manganese being but very feeble, the latter is liberated by the action of heat; the employment of this salt is therefore a useful roundabout way of introducing oxide of manganese into the oil.

As non-oxidised metallic lead, in a very porous condition, increased the drying properties of the oil, it was interesting to study the action upon oil of other metals capable of being easily precipitated. But the oil dried no quicker when treated with precipitated tin or copper. Besides, these results might have been foreseen, for Chevreul showed that linseed oil, spread upon well-polished lead, dried much more rapidly than when spread upon copper, brass, zinc, or iron. With these metals the oil did not dry any faster than upon plates of glazed or unglazed porcelain, glass, or plaster of Paris. As to the numerous other substances besides the salts of manganese and lead proposed to be added to drying oils to hasten their drying properties, none of them appear to exert any beneficial influence. Chevreul made a comparative study of the oxides of zinc and lead and showed that the former had no appreciable influence, and that certain substances even acted in a contrary manner, retarding instead of hastening the drying of the oil, such as the oxide of antimony and antimonious arseniate. If certain substances *appear* to act as driers, the reason is to be found in the fact that they have been used in conjunction with the application of heat, and their apparent beneficial action is due to the heat alone. According to Andés the following substances may be regarded as *absolutely useless:* all organic matters (sepia, dog excrement, bread, onions, garlic), red oxide of mercury, verdigris, lime, brass, zinc, alum, hydrated oxide of iron, boracic acid, oxide of antimony, gypsum, vermilion, pumice-stone, animal charcoal. The following as *Oxidising Agents.*—White lead, sulphate of lead, carbonate of lead, basic acetate of lead, black oxide of manganese, hydrate of protoxide of manganese, sulphate of zinc, oxide of zinc, umber, and those in this final list as *Energetic Oxidising Agents.*—Air—acting through its oxygen—red lead, litharge and the different oxides of lead, borate of manganese and the hydrated peroxide of manganese.

Kastner has proposed the plumbates of the alkaline earths as driers. These are prepared by heating in a suitable furnace two molecules of baryta, strontia, or lime, or their corresponding carbonates with one molecule of oxide of lead. The plumbate of baryta is dense black, that of strontia, brown, and that of lime, bright red. Kastner is of opinion that the drying property of the oil is increased by the richness in oxygen and the introduction of lead; he holds further that the introduction of the alkaline earths themselves may produce oleates, which after drying assume a consistency of remarkable elasticity. *We ought therefore to confine ourselves in the use of driers to lead and manganese, to their oxides, and in certain cases to some one of their salts.*

Catalytic Action of Driers.—An experiment of Chevreul lends support to the theory of looking upon manganese and lead as simply performing the function of intermediaries or oxygen carriers, viz.: If we make a mixture of raw linseed oil and manganese-boiled oil, the liquid resulting from this mixture has a much greater oxygen absorbing power than either of the liquids constituting the mixtures taken separately.

If this be true, then a pale boiled oil made by diluting a manganese-boiled oil with raw oil ought to be a very desirable mixture indeed.

It follows that the quantity of oxygen absorbed during the same period of time is not proportional to the quantity of oxide of manganese contained in the oil, since the boiled oil reduced with raw oil absorbs more oxygen, although bulk for bulk it contains less oxide of manganese than the original manganese-boiled oil. The only feasible explanation is this: If the raw oil in the mixture absorbs a greater quantity of oxygen in the same space of time, it is simply because this oxygen is supplied to it under more favourable conditions. Now these conditions are precisely the fixation of oxygen by the oxide of manganese, which forthwith gives it up to the oil; there is thus a continual transport of oxygen from the air to the manganese and thence to the oxidisable principles of the oil.

It seems, therefore, that an oil will dry in a better manner the less metallic linoleate it contains, because linoleate of lead absorbs less oxygen than linolein and becomes brittle; all we have to do is to introduce a quantity of lead or manganese sufficient to extract from the air the quantity of oxygen necessary to oxidise the linolein as fast as this oxidation proceeds. A large quantity of lead or manganese does not hasten the oxidation—the intensity of which is the sole function of the drying quality of the oil used—but would on the contrary yield a less elastic and slower forming final product. Again, summing up the proper conditions under which the drying properties of an oil are accelerated, we can deduce the following principle (1) the oil ought to be refined and clarified; (2) there is an advantage in allowing the oil to age before using it. If need be oxidation may be started; (3) it is more profitable to use boiled oil than raw oil; (4) the drying of raw oil or boiled oil is hastened by the addition of either lead or manganese or cobalt compounds in known quantities or by metallic lead in a fine state of division. It remains to be considered how in actual practice we can conform to the principles enunciated. The oxides of lead or manganese or cobalt or their salts are preferred. But the use of metallic lead has latterly been tried with promising results.

Treatment of Linseed Oil with Driers in the Cold—Driers are generally incorporated with the oil by aid of heat. However, interesting attempts have been made to effect this result in the cold. Numerous attempts are made to prepare quick-drying oils in the cold, thus securing economy and a paler oil. Few processes have, however, been published. The simplest plan consists in running the oil into a reservoir, from whence it falls upon plates superimposed at alternating inclinations and at certain distances one from another. The oil thus runs in a thin layer in a zigzag course from one plate to another and thickens as it absorbs oxygen; by using lead plates the action is more rapid. The oil when it reaches the bottom of the column of plates is pumped up to the top, and the same process is gone through again, and so on until the oil has assumed the requisite consistency. The theory of this is very simple—the oil oxidises, generates fatty acids which attack the lead, and the resulting nascent linoleate of lead dissolves in the oil.

1. *Bink's Method. The First Attempt at Blowing Linseed Oil.*—In Bink's process a very small quantity of drier, 0·2 to 0·6 per cent., consisting of a mixture of manganese oxide and a lead salt, is first added to the oil, then a current of air passed through until the desired quantity of oxygen is absorbed. But this does not give satisfactory results without the aid of a moderate heat.

2. *Bouis' Process.*—Bouis introduced lead oleate into the oil; the product is colourless and dries satisfactorily. It has been proposed later to replace the oleate by the linoleate of lead, but the latter, it is said, does not give the same result, as it is said to be insoluble in oil in the cold. Hartley and Blenkinsop dissolve the manganese linoleate in naphtha and introduce it in solution in that vehicle into the oil and then blow air through it. But according to Professor Sabin, this process was well known in America long before Hartley, etc., patented it. Moreover, the writer recommended it in his Polytechnic lectures several years before Hartley's patent. See Vincent's method of oil boiling.

3. *Liebig's Method.*—Liebig recommended the agitation of the oil with water, litharge, and basic acetate of lead. The latter salt is prepared by grinding as finely as possible 1 part of acetate of lead with 1 part of litharge to thorough incorporation, and placing the mixture in a porcelain basin, which is heated on the water-bath and covered with another porcelain basin to prevent access of air. After an hour's heating a white mass is obtained, which is triturated with 5 parts of water. The solution on standing and clarifying contains the basic acetate of lead. It is diluted with its own bulk of water, and vigorously shaken with 20 parts of oil which has been triturated with 1 part of finely ground litharge. The mixture thus obtained is added to the oil to be treated, which it soon decolorises, and at the same time stimulates its drying properties. In those cases where the presence of lead would be prejudicial to the object for which the oil is to be used, it is agitated with a small quantity of sulphuric acid diluted with 3 parts water. The lead may also be eliminated by agitating the oil with a salt of manganese, the acid of which forms an insoluble lead salt—the sulphate, for example, or, better, the borate.[1]

4. *Livache's Process.*—Livache's process consists in agitating the oil in the cold with finely divided metallic lead, perfectly free from oxide. For this purpose he uses the spongy lead obtained by precipitating a lead solution by zinc plates. For 1000 gallons of oil, 30 lb. nitrate of lead are dissolved in 15 gallons of water; about 1 ounce of nitric acid is added, then 6 lb. of sheet zinc. The precipitated lead is placed in capacious funnels, plugged with shavings, or, better still, with sea-weed, where it is rapidly washed with water; then a small quantity of oil is poured on very gently, so as to displace the water imbibed by the porous mass of precipitated spongy lead. When the oil runs away clear and limpid from the bottom of the funnel, and as a consequence thereof all the water has been displaced, the mud thus obtained is run into the tank containing the 1000 gallons of oil, that is nearly 20 tons, where the whole is subjected to

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[1] Liebig's method is regarded by some as simply a method of refining the oil. It was all Liebig claimed for it.—J. G. M.

agitation. In working with small quantities the requisite agitation may be imparted by running the oil and lead into a cask, and rolling it about from time to time on the floor. The oil thus treated assumes a reddish tint, which disappears as soon as it oxidises in contact with air. If the treatment has been efficient, the resulting oil is as fluid as the original, contains a small quantity of lead, and dries in 24 hours in the open air. The rationale of this process is easily seen, the fatty acids originally present in the oil act on the finely divided metallic lead, and the nascent linoleate of lead, aided by the heat produced by its formation, dissolves in the oil as soon as formed. It is advisable to introduce manganese into the oil prepared in this way. A salt of manganese very soluble in oil, viz. the nitrate, is added, say, 15 lb. for the proportions given, and the whole frequently stirred for two or three days, after which it is allowed to stand and decanted. If this oil were at once used, as it often contains an excess of nitrate of manganese, which deliquesces in the air, it might dry dull. To obviate this, 7½ lb. of dry precipitated oxide of lead are added, and the whole again subjected to agitation. After standing a perfectly clear oil is obtained, which, exposed to the open air in a thin layer, at the ordinary temperature, dries in 6 hours. During drying the absorption of oxygen produces, in consequence of the presence of oxide of manganese, a brown coloration, but the latter soon disappears, and finally a beautifully brilliant, perfectly dry and completely colourless coat is obtained. Some manufacturers using this process have found the oil in certain cases to be tacky, perhaps owing to the presence of a small quantity of glycerine. This has led them to heat the oil treated first with finely divided lead and then with a salt of manganese, and it would appear that they have obtained very interesting results.

Boiling Oil Through the Bung-Hole.—The American process of boiling oil in the cold, or, as they term it boiling oil through the bung-hole, consists in simply dissolving fused linoleate of lead or manganese, or their rosinates, in spirits of turpentine or naphtha, and adding a certain amount of this solution to each barrel of raw oil. The painter does the same thing when he adds "terebine" to his paint.

The figures in table give, Col. I., the amount of metal, whether lead or manganese, in certain well-known driers, the weight, Col. II., per ton of oil, and the temperature of incorporation. The temperature at which the drier dissolves, Col. III., should never be exceeded, except to hasten the process in a rational manner (Weger)

TABLE GIVING INFORMATION AS TO USE OF DRIERS IN OIL BOILING.

Drier.	I. Percentage of Metal in Commercial Product.	II. Lb. per Ton of Oil.	III. Temperature Degrees C.[1]
Manganese peroxide, MnO_2	30-60 Mn	—	250
Hydrated manganic oxide, $Mn_2O_3H_2O$	45-50 ,,	4½	180-200 better 200-220
,, manganese peroxide, MnO_2H_2O	45-50 ,,	1½	
Litharge, PbO	93 Pb	—	150 generally higher
Manganese borate	15-20 Mn	11-22	In the cold generally 200 and higher
,, ,, commercial	5 Mn	up to 66	
Precipitated manganous rosinate	7	22-33	In the cold generally 130-150
Fused manganic rosinate	4	66	
Linoleate of manganese	10	22	
Lead manganese rosinate	8-10 Pb 1-2 Mn	44-66	

Patent Driers: Concentrated Driers and Liquid Driers.—*Concentrated driers* consist of the product obtained by heating linseed oil at 250° to 300° C. to the consistency of sticking plaster, with a quantity of litharge, red lead, borate of manganese greater than 10 per cent. and even as high as 70 per cent. of the weight of the oil. Sugar of lead, oxide of zinc, etc., are added to or partially substituted for the preceding substances.

Concentrated driers consist of a thick viscous mass, generally of a deep brown colour composed essentially of fused linoleate of lead. A good product may be made by boiling in a small pot 7 parts (by weight) of good and aged linseed oil—old baked oil—with a mixture of 2 parts of litharge in powder and 2 parts of red lead. The oil at first assumes a beautiful red colour, which turns brownish as the temperature rises. Suddenly it thickens, looking like bronze in fusion, whilst at the same time abundant fumes are given off. A sample drop spotted on a glass plate should become in a minute perfectly solid, with no viscosity nor tackiness whatever. It is thinned down with spirits of turpentine or rectified naphtha to the requisite consistency when required for use. Concentrated driers dissolved in benzol or spirits of turpentine are used to make "boiled"

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[1] To bring to degrees Fahrenheit × 9 ÷ 5 + 32 = e.g. $250° \times 9 = \frac{2250}{5} = 450 + 32 = 482°$ F.

TABLE OF METALLIC OXIDES AND SALTS USED AS DRIERS.

Drier.	Chemical Formula.	Molecular Weight.	Theoretical Percentage of Metal.	Average Percentage of Metal in Commercial Products.	Colour.	Temperature at which Product Yields Good Drying Oil.
						° C.
Litharge	PbO	223	92·8	Up to 93	—	
Red lead	Pb_3O_4	685	91·2	Up to 91	Red	
Lead acetate	$Pb(C_2H_3O_2)_2 + 3H_2O$	379	56·2	56·2	White	
Manganese dioxide	MnO_2	87	63·22	(30 60) 55	Black	*ca.* 250
Hydrated peroxide of manganese	$Mn_2O_3 . H_2O$	176	62·50			170-200,
Manganic hydroxide	$MnO_2 . H_2O$	105	52·38	35-55		
Manganous ,,	$MnO . H_2O$	89	61·80			200-220
,, chloride	$MnCl_2 . 4H_2O$	198	27·78	*ca.* 27	Pink	*ca.* 250
,, sulphate	$MnSO_4 . H_2O$	169	32·51	27 31·5	White	over 250
Manganese nitrate	$MnN_2O_6 . 6H_2O$	287	19·16	19-20	Rose	150-170
Basic manganese chromate	$MnO . MnCrO_4 . H_2O$	260	42·30	38-45	Black	200
Manganous borate	?	?	?	(5-22) 15	White	
,, carbonate	$MnCO_3 . H_2O$	133	41·35	41-42	Pale brown	*ca.* 280
,, oxalate	$MnC_2O_4 . 2H_2O$	179	30·37	*ca.* 30	White	over 280
,, succinate	$MnC_4H_4O_4 . 4H_2O$	243	22·63	22·5	Pale lake	*ca.* 270
,, citrate	$Mn_3(C_6H_5O_7)_2 . 9H_2O$	705	23·40	22·0	White	,,
,, tartrate	$MnC_4H_4O_6 . 2H_2O$	239	23·01	23·0	Pale lake	over 270
,, benzoate	$Mn(C_7H_5O_2)_2 . 4H_2O$	309	14·90	14·8	,,	*ca.* 200
,, formate	$Mn(CHO_2)_2 . 2H_2O$	181	30·38	29·7	Pale violet	*ca.* 270
,, acetate	$Mn(C_2H_3O_2)_2 . 4H_2O$	245	22·45	22	Pink	120

oil or oil "boiled through the bung-hole" in the cold from raw linseed oil.

Terebine or liquid drier is made like concentrated driers, but when the pot is taken off the fire it is only allowed to cool for a few minutes, when it is thinned down with successive additions of spirits of turpentine, with constant stirring. It is then passed through coarse linen, and stored in closed vessels. Liquid driers consist therefore of linseed oil saponified and oxidised to a greater or less extent, i.e. heated until it will roll into pills, and afterwards dissolved in spirits of turpentine. There are numerous recipes for making driers; *inter alia*, the following:—

Oil and Solids in Lb. Turps in Gallons.	Concentrated Driers.				Pale Liquid.			Driers.				Terebine.		
Linseed	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Boiled oil	4	—	—	—	—	—	—	—	—	—	—	—	—	—
Litharge	2	2	—	1	—	—	—	2	—	—	—	—	—	—
Sugar of lead	—	—	2	1	1½	—	1½	1	—	2	1	1½	—	—
Red lead	2	1	2	—	—	—	—	2	1	2	—	—	—	—
Black oxide of manganese	—	2	—	1	—	—	—	—	2	—	1	—	—	—
Manganese borate	—	—	—	—	—	2	2	—	—	—	—	—	—	—
Zinc sulphate dehydrates	—	—	—	—	—	—	—	—	—	—	—	—	2	2
Umber	—	—	—	1	—	—	—	—	—	—	1	—	2	1½
Shale brown	—	—	—	—	—	—	—	—	2	—	1	—	—	—
White lead, pure dry	—	—	—	—	3	—	—	—	—	—	—	3	—	—
Zinc white	—	—	—	—	—	2	—	—	—	—	—	—	—	—
Turps in gallons	—	2	2	2	2	2	2	2	2	—	2	2	2	2

In the manufacture of white liquid driers the mass does not become red on boiling, but white at first, and afterwards a very faint yellow. Liquid driers are but little used for white colours —solid driers are preferred; but with other coloured paints very rapid drying is effected by simply adding, say, a few parts in 100. Complaints are made that certain driers when added to linseed oil in solution as liquid driers fall out of solution after a longer or shorter period of time. Sometimes, however, these complaints will not bear investigation. Endeavours have been made by working in the cold to produce very pale liquid driers. One variety which is used very extensively is made by intimately mixing 100 parts (by weight) of finely pulverised sugar of lead with 1200 parts (by weight) of poppy-seed oil. This mixture is exposed to sunlight in a glass vessel and frequently stirred. There is got in this way a perfectly colourless oil, which, when thinned down with 250 parts (by weight) of spirits of turpentine, dries very rapidly, yielding a solid, durable coating. *Hartley and Blenkinsop's drier* consists of zinc oxide mixed with a solution of linoleate of manganese dissolved in naphtha. One per cent. of manganese linoleate added to linseed oil in a dilute naphtha solution renders it quick drying. There is no necessity to blow air through it. The air will do its work very well after the oil is applied to any given surface.

Terebine.—The so-called "terebine" very often consists simply of japanners' gold size thinned down with spirits of turpentine. Japanners' gold size is linseed oil boiled with litharge, red lead, sugar of lead and zinc sulphate until it will roll into pills, and then dissolved in spirits of turpentine. Another process consists in fusing 2 parts of Manilla copal, which is then mixed with ½ part of linseed oil and 6 parts of concentrated driers made by one of the formulæ given above, after which the whole is incorporated with 14 parts of spirits of turpentine. The bulk of the *paste* "patent driers" used in the trade consist of 90 per cent. or more of a mixture consisting of equal quantities of chalk, "Paris white," and barytes, and about 10 per cent. or less of actual driers. When it is desired to prevent the paint from cracking, very good results are obtained by using spirits of turpentine which has simply been shaken up with litharge and decanted. A liquid is thus obtained which does not affect the colour, and which also gives a very durable coating.

Hannay's glycl lead linoleates and basic lead linoleates, made by dissolving about 2 parts (by weight) of litharge in 1 part of linseed oil at as low a temperature as practicable, should make excellent driers either *per se* or in turps or benzene.

THE MANUFACTURE OF DRIERS.

The principal substances used as "driers" or aids in oil-boiling are metallic lead, Pb = 207, oxides and salts of (A) lead, (B) manganese, and (C) cobalt.

Lead Compounds Used as Driers.[1]—(1) Litharge; (2) red lead; (3) acetate or sugar of lead; (4) lead borate; (5) lead rosinate; (6) lead linoleate, and either of the last two or both mixed with either manganese rosinate or linoleate or with both.

1. *Litharge*, PbO = 223; Pb = 92·83; O = 7·17 per cent. *Manufacture.*—When metallic lead is heated in a current of air, it is oxidised into massicot, PbO(Pb + O = PbO 207 + 16 = 223). 207 parts of oxidised lead yield 223 of massicot. When this massicot is further heated, it fuses, and the fused product after cooling is known as litharge, or, from its scaly nature, as *flake* litharge. It does not, however, undergo any chemical change. When buying litharge for use as a drier, it should be guaranteed free from massicot, also copper, which is often present in considerable quantity, and acts injuriously. Moreover, it should not contain unconverted metallic lead nor sand nor silver.

Properties.—Litharge should dissolve completely in dilute nitric acid and in acetic acid to a colourless solution. A green coloration would indicate copper. Any residue in either of these acids will consist, most probably, of sand or grit, or possibly of lead peroxide (PbO_2); acetic acid may leave a residue of non-oxidised blue lead. When litharge is heated with linseed oil for some time at the temperature at which that oil is said to "boil," but, more properly, at which it undergoes destructive distillation, it dissolves in the oil. In varnish-making and oil-boiling it is often found at the close of the operation reduced to metallic lead and the superincumbent oil, etc., has perforce been oxidised, *pro rata*. In such cases without doubt all its oxygen is seized hold of and absorbed by the "boiling" oil. Litharge assists in oil-boiling in three different ways: (1) It may combine with any free linoleic acid in the oil at a comparatively low temperature to form linoleate of lead, which will dissolve in the oil under favourable circumstances; (2) at a higher temperature it will eliminate glycerine from the oil and oxidise the latter to acrolein, and combine with the liberated linoleic acid to form linoleate of lead, which will again dissolve in the oil under favourable conditions; (3) in the act of being reduced to metallic lead, it will part with its oxygen to the oil, and consequently by starting the oxidation process increase the drying properties of the oil. The drawback attendant on the use of litharge and all lead salts as driers is the dark colour which they impart to boiled oil, due no doubt to the dissolved lead linoleate. This dark colour is intensified by the great heat at which the oil must be kept for some considerable time before the litharge dissolves and plays its part. Another drawback attendant on the use of litharge and other lead salts is that the oil or varnish into which they enter cannot be used in conjunction with or in juxtaposition to pigments consisting of or containing sulphides liable to combine with lead compounds to form the black sulphide of lead. Sulphur emanations act similarly. Paintings or decorations injured in this way may, it is said, be revivified by washing with a weak solution of peroxide of hydrogen, which converts the black sulphide of lead into white sulphate of lead without materially affecting the painting in any other way. But this is erroneous. Thenard only used it to restore a white lead background, in a black crayon drawing, of Raphael. Such delicate colours as madder lake would be destroyed by hydrogen peroxide. This black coloration is very often due to the free sulphur contained in the pigment, and not to the combined sulphur, which, looked at from a rational point of view, must be regarded as more or less stable. On the other hand, linseed oil boiled over the naked fire with litharge gives an elastic, durable coat of greater lustre and less susceptible to dry superficially than manganese-boiled oil. In a word, litharge-boiled oil is more of the nature of a varnish than manganese-boiled oil.

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[1] Galen (A.D. 131-200) states that "white lead and litharge thicken and dry".—"De Meth. Med.," iii., 4.

The Pharmaceutical Society requirements for litharge are that:—

"It shall dissolve completely in dilute nitric acid (1 : 4) and also in acetic acid (B : P), and shall give no characteristic reaction on being tested for copper, iron, and carbonates."

Twelve samples of litharge were obtained by Remington from leading manufacturers of this material, and were analysed, with the following results:—

lead and zinc sulphate until it will roll into pills, and then dissolved in spirits of turpentine. Another process consists in fusing 2 parts of Manilla copal, which is then mixed with ½ part of linseed oil and 6 parts of concentrated driers made by one of the formulæ given above, after which the whole is incorporated with 14 parts of spirits of turpentine. The bulk of the *paste* "patent driers" used in the trade consist of 90 per cent. or more of a mixture consisting of equal quantities of chalk, "Paris white," and barytes, and about 10 per cent. or less of actual driers. When it is desired to prevent the paint from cracking, very good results are obtained by using spirits of turpentine which has simply been shaken up with litharge and decanted. A liquid is thus obtained which does not affect the colour, and which also gives a very durable coating.

Hannay's glycl lead linoleates and basic lead linoleates, made by dissolving about 2 parts (by weight) of litharge in 1 part of linseed oil at as low a temperature as practicable, should make excellent driers either *per se* or in turps or benzene.

THE MANUFACTURE OF DRIERS.

The principal substances used as "driers" or aids in oil-boiling are metallic lead, Pb = 207, oxides and salts of (A) lead, (B) manganese, and (C) cobalt.

Lead Compounds Used as Driers.[1]—(1) Litharge; (2) red lead; (3) acetate or sugar of lead; (4) lead borate; (5) lead rosinate; (6) lead linoleate, and either of the last two or both mixed with either manganese rosinate or linoleate or with both.

1. *Litharge*, $PbO = 223$; $Pb = 92 \cdot 83$; $O = 7 \cdot 17$ per cent. *Manufacture.*—When metallic lead is heated in a current of air, it is oxidised into massicot, $PbO (Pb + O = PbO \; 207 + 16 = 223)$. 207 parts of oxidised lead yield 223 of massicot. When this massicot is further heated, it fuses, and the fused product after cooling is known as litharge, or, from its scaly nature, as *flake* litharge. It does not, however, undergo any chemical change. When buying litharge for use as a drier, it should be guaranteed free from massicot, also copper, which is often present in considerable quantity, and acts injuriously. Moreover, it should not contain unconverted metallic lead nor sand nor silver.

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For metallurgical determinations the litharge used should of course be free from silver.

2. *Red Lead Minium*, 2PbO, $PbO_2 = Pb_3O_4 = 685$; Pb = 90·2; O = 9·8 per cent. *Manufacture.*—Red lead Pb_3O_4 is made by heating litharge in contact with air at 300° C., a temperature slightly below its point of fusion. The litharge should be free from copper. It gradually becomes converted into a fine red known as red lead. The manufacture of red lead is a Derbyshire industry, and the process of the present day differs in no essential particulars from that described so vividly by Bishop Watson 125 years ago. A variety of red lead, made by igniting white lead, is sold as orange lead. Although dearer in price it is no more efficacious as a drier than ordinary red lead. It always contains undecomposed carbonate.

Composition.—The red leads of commerce differ in composition according to the length of time they have been furnaced. However, the proportion of oxygen absorbed by the litharge never exceeds that which corresponds to the formula 2PbO, $PbO_2 = Pb_3O_4$. When red lead is heated it darkens, and then, at a temperature above 300° C., it gives off oxygen, becoming reconverted into litharge. *Test for Purity.*—When red lead is treated with nitric acid the two equivalents of PbO are dissolved as nitrate of lead, leaving the PbO_2 behind as a puce-coloured residue which is perfectly insoluble in nitric acid, and only dissolves in dilute nitric acid after it has been reduced by the addition of oxalic acid. When this reagent is introduced into the test tube, containing the nitric acid and red lead, vigorous action ensues, the whole of the puce-coloured oxide being converted into white crystalline nitrate, to which it is only necessary to add a little boiling water for complete and instantaneous solution. Any residue remaining is generally barytes. Sophistication with ground brick is only met with in books. Red lead containing more oxygen perhaps in a more available state, is a more energetic drier than litharge, and its function as a drier is similar to what it plays in a storage battery.

Other Uses.—Besides its use as a drier, red lead is used in the manufacture of matches, wall paper, sealing wax, crystal glass; mixed with white lead in oil it is used to form a cement for steam joints. Red lead "substitutes" are of little or no use as driers.

N.B.—2A. *Peroxide of Lead.* — The puce-coloured peroxide of lead neither acts as a drier nor a catalyst in regard to linseed oil. It retards drying and this fact is an insuperable stumbling-block to the peroxide theory of oil-boiling. This inertia may quite easily be explained by assuming that the affinity of the peroxidic oxygen for lead monoxide is greater than for oil.

The Use of Red Lead as a Paint Material.—It is interesting to know how a substance used as a drier behaves as a paint when ground in oil. Red lead is regarded as one of the best, as shown in the Havre de Grace bridge tests, but to come to a correct conclusion it is necessary to know the composition of the paint and also that of the red lead employed. It has been maintained that a red lead containing 95 per cent. of Pb_3O_4 yielded the best protective paint, but from experiments carried out by the Institute of Industrial Research at Washington this does not appear to be the case, better results being obtained with those containing only 86 to 90 per cent., and the specifications of the United States Navy have now been altered accordingly. Gardner is of opinion that pure red lead does not react appreciably with linseed oil, and therefore the paint remains soft for a considerable time, a certain proportion of litharge must be present in the pigment to react with the oil and form a hard and durable film. This litharge must be in the pigment when it is manufactured, as no amount of mixing would suffice to incorporate litharge with red lead after it had been made. A new orange mineral which has recently been placed on the market is a fume pigment so flocculent that it occupies double the volume of red lead and yields a paint which is extremely smooth, durable, and elastic. This pigment is extremely suitable for reducing para reds for pigment manufacture. Ordinary red lead is crystalline, when the crystals are broken up by grinding it turns yellow; so delicate are these crystals that 10 per cent. of barytes cannot be added to red lead without reducing the colour a hundred fold.

3. *Lead Acetate (Neutral)*, $Pb(C_2H_3O_2)_2 + 3H_2O$. *Sugar of Lead. Molecular Weight* 379.—This salt was formerly known as *salt of Saturn*, or sugar of Saturn. It is prepared by neutralising acetic acid with litharge. It crystallises in oblique rhomboidal prisms, colourless, transparent and efflorescent. It is generally met with in the form of heavy compact crystalline masses, somewhat resembling loaf-sugar. Its odour is acetous, whilst its taste is both sweet and astringent, its after taste is bitter and disagreeable. It dissolves in ½ part of cold water and in 8 parts of alcohol. Its solution slightly reddens blue litmus paper, and is partially decomposed by carbonic acid, which at the same time liberates a small quantity of acetic acid, which preserves the rest of the salt from the action of carbonic acid.

Action of Heat on Lead Acetate.—Crystallised acetate of lead melts at 75·5° C., at 100° C. it loses water and a small quantity of acetic acid. It afterwards solidifies, but towards 280° C. it again melts. The dehydrated salt would appear to consist of a sesquibasic acetate. At higher temperatures it decomposes with disengagement of carbonic acid, acetic acid and acetone, leaving a residue of very finely divided and highly combustible metallic lead. Lead acetate is a very energetic drier; perhaps much of the metallic lead found by varnish-makers at the bottom of their pots may come from the complete reduction of the acetate and not from the litharge often used in conjunction with it.

3A. *Basic Lead Acetate.*—The so-called neutral lead acetate just described results from the combination of two equivalents, i.e. 120

parts of monobasic acetic acid with one equivalent, i.e. 223 parts of the di-acid base litharge. When *two* equivalents of a *monobasic* acid, e.g. acetic acid, combine with *one* equivalent of a *di-acid* base, e.g. litharge, a neutral or normal salt is produced. But it is found in actual practice that certain neutral or normal salts, in their state of solution in water, can still dissolve and combine with a further proportion of base. Thus when one equivalent of neutral acetate of lead is dissolved in water, it combines on boiling with an additional equivalent of litharge to form the di-basic salt, $PbA_2Pb(HO)_2$, basic acetate of lead. By digesting together one equivalent of sugar of lead with two equivalents of litharge the tribasic salt, $Pb(A)_2 2Pb(HO)_2$, is produced. These basic acetates, owing to the fact that their excess of litharge, or, rather, lead hydrate, PbO, H_2O, is in a loose state of combination, easily give up this excess to weak acids, even carbonic acid, as exemplified in the manufacture of white lead. Should raw linseed oil contain free "linoleic acid," agitation with a solution of basic acetate of lead will convert the former into linoleate of lead, and if the agitation be renewed from time to time this linoleate of lead will dissolve to some extent in the oil, imparting drying properties thereto, whilst the insoluble magma produced by the action of the basic acetate on the colouring matter and mucilage collects as an insoluble slime at the bottom of the vessel. Such is the principle of the refining of linseed oil by Liebig's method and the imparting of drying properties thereto in the cold by means of basic acetate of lead, a substance the utility of which is not appreciated either by the varnish-maker or colour-maker to the extent to which its intrinsic merits entitle it.

4. *Lead Borate*, $Pb(BO_3)_2 + H_2O = 310{\cdot}8$.—Precipitated borate of lead is a white substance made by precipitating the boracic acid in 382 parts (i.e. one equivalent) of borax ($Na_2B_4O_7$ + 10 aq.) by one equivalent of a lead salt—that is to say, 331 parts of nitrate of lead $Pb(NO_3)_2$ or 379 parts of neutral acetate of lead ($Pb(C_2H_3O_2)_2$ + 3 aq.). The mother liquor is filtered off, the precipitate is well washed, filter-pressed, and dried in the usual way. This substance combines the drying properties of both lead and boric acid. It is said not to darken the oil to quite the same extent as other lead driers, but a sample inspected by the author was the darkest sample of boiled oil he ever saw. Possibly the darker colour was due to the operator. Meurant, German patent 223,754, prepares lead borate for use as a drier by fusing boric acid and litharge together in molecular proportions.

5. *Rosinate of Lead*.—The first stage in making rosinate of lead, erroneously termed resinate of lead, is the preparation of an alkaline solution of rosinate of soda. Rosin being an acid of variable degrees of acidity, different samples require different proportions of caustic alkali for neutralisation. The best plan is to add rosin gradually with constant stirring to a very dilute boiling solution of caustic alkali of known strength until the latter is exactly neutralised.

Starting from the data that every 62 parts of anhydrous sodium oxide (real alkali) present in solution as rosinate of soda require for complete precipitation one equivalent of a lead salt, viz. 379 parts lead acetate or 330 parts lead nitrate, and knowing the original bulk of the alkaline solution used and its richness in real alkali, as determined by the hydrometer and the usual tables, it is easy to calculate the amount of lead salt necessary to displace the soda in the solution of alkaline rosinate by lead, and thus throw down all the rosin as rosinate of lead.

The dilute solution of the proper proportion of lead salt is gradually added with constant stirring to the equally dilute solution of alkaline rosinate; the mother liquor is syphoned off, the precipitated lead rosinate, which is further well washed, drained and dried. It may be heated to incipient fusion to expel water.

6. *Linoleate of Lead.*—Linoleate of lead is made by precipitating a solution of linseed oil soft soap, made by saponifying linseed oil with caustic potash in the usual way. 100 lb. of linseed oil on an average require 19½ lb. of pure caustic potash, equal to 16½ lb. of anhydrous potassic oxide, for complete saponification (see Sap. Numbers). Caustic potash is sold as containing so much per cent. of anhydrous caustic alkali; when pure it contains 83·9 per cent. It is, therefore, a mere matter of calculation, if 100 lb. of linseed oil require 19½ lb. of caustic potash, when the strength is 83·9 per cent., to find how much will be required for complete saponification when the strength is 80 (or any other figure) per cent. The soap is dissolved in five or six times its weight of water, and the linoleic acid precipitated therefrom by a dilute solution of a lead salt. The exact proportion of lead salt for complete precipitation depends upon the amount and the strength of the caustic alkali used. 112·2 parts of pure caustic potash, equal to 94·2 parts of anhydrous potassic oxide, require one equivalent of a lead salt, say 379 parts lead acetate or 330 parts lead nitrate. The lead salt solution is added gradually to the soft soap solution with constant stirring. The mother liquor is syphoned off the precipitated lead linoleate, which is then further washed, drained and dried. Heat after drying to incipient fusion to expel last traces of water.

Pyrolusite. Peroxide of Manganese, MnO_2.—This is the oxide which most commonly occurs *native*, and is resorted to as the source of the other combinations of this metal. In this country it is common in Devonshire, Somersetshire, and Aberdeenshire. It is found in a variety of forms: compact and massive, pulverulent and crystallised. a vey of the latter varieties have a grey metallic lustre, and are found varnisrly radiated, and in rhomboidal prisms. Its specific gravity plete retween 4·8 and 4·9. It is the *pyrolusite*[1] of mineralogists.
conjui

3A. [1] = *fire*, and λύειν = *to set free*, or *loosen*: from the facility with which part describ ygen is expelled by heat: or, according to Graham, from πύρ and λούειν to n its use in discharging the colour of glass.

The following analyses of five samples of native peroxide of manganese are given upon the authorities of Berthier (I., II., III.), Klaproth (IV.), and Turner (V.).

ANALYSES OF NATIVE (PEROXIDE OF MANGANESE) PYROLUSITE.

	I.	II.	III.	IV.	V.
Peroxide of manganese	93·8	84·0	72·7	99·5	97·8
„ „ iron	1·0	2·0	1·0	0·0	0·0
Oxide of copper	trace	trace	trace	0·0	0·0
Carbonate of lime	0·0	9·0	24·0	0·0	0·0
Silica	4·0	4·0	1·2	0·0	0·5
Baryta	0·0	0·0	0·0	0·0	0·5
Water	1·2	1·0	1·1	0·5	1·2
	100·0	100·0	100·0	100·0	100·0

Under the name of *manganese*, this substance is met with in commerce, and is largely consumed in the manufacture of bleaching agents. In the laboratory, it is resorted to as a source of oxygen gas, $2MnO_2 = Mn_2O_3 + O$, for which purpose it should be well dried previous to introducing it into the retort: sometimes it is mixed with carbonaceous matter, and then yields carbonic acid: it also generally gives off a little nitrogen upon the first application of heat, the source of which is not obvious. Carbonate of lime, silica, oxide of iron, and some other substances, are, as the above analyses indicate, not infrequently present, and lower its value *pro rata* associated with it. In the arts it is used to give a black colour to earthen-ware, and to remove the green colour which glass derives from protoxide of iron; for this purpose it is added in such quantity only as to peroxidise the iron, by becoming itself protoxide, and neither the peroxide of iron nor the protoxide of manganese, which remain, materially interfere with the colour of the glass: in this case, MnO_2, acting on $2FeO$, produces MnO and Fe_2O_3. A little excess of oxide of manganese is apt to give the glass a pink tint, which as is sometimes seen in plate glass windows, does not appear till after long exposure to light. This oxide is also said to sweeten foul water, or to prevent its becoming putrid. It usually loses weight (water), on being dried at a temperature not exceeding 300°; at a red-heat it becomes sesquioxide; and, intensely heated in an iron tube, or with a minute quantity of carbonaceous matter, part of it becomes protoxide. It is not altered by air or water. It is a good conductor of electricity. It forms no combinations with the acids; but such of them as appear to dissolve it, reduce it to the state of protoxide. Gently heated with hydrochloric acid, chlorine is liberated, in consequence of the decomposition of the acid by the oxygen of the oxide. $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. Boiled with sulphuric acid, oxygen is evolved, and a soluble sulphate of the protoxide is formed, [$MnO_2 + SO_3 = MnO, SO_3 + O$], together with a small portion of manganic acid, (which gives the solution a pink colour and bleaching properties?) Nitric acid does not attack it unless it contains sesquioxide, or some deoxidising agent be at the same time present. Many vegetable acids decompose it by the aid of heat.

As binoxide of manganese is extensively used by the bleacher, and as it occurs of various degrees of purity in commerce, a ready mode of determining its value, or in other words, the quantity of oxygen per cent. which it contains, is desirable: this may be effected in various ways, but it is generally attained by ascertaining its power of decomposing hydrochloric acid and evolving chlorine: to this end the oxide to be tested is mixed with hydrochloric acid, and heated, and the evolved chlorine is received into a jar containing lime diffused through water, by which a chloride of lime is formed; the quantity of chlorine is then determined by the process already described. Other modes of testing this oxide have been suggested (see Kane's "Elem. Ch.," 580. Graham, 536. Levol, "Chem. Gaz.," April, 1843).

Pure peroxide of manganese is sometimes useful as a test of the presence of iodine, bromine, and chlorine: when mixed with a salt containing iodine, and the mixture heated with a little sulphuric acid, the violet vapour of iodine is evolved; the salts of bromine give in the same way a brown vapour; and from the chlorides chlorine is evolved.

Sulphate of Manganese. Manganous Sulphate.—This beautiful rose-coloured salt is formed, (1) by dissolving the protoxide or protocarbonate in dilute sulphuric acid, and evaporating; (2) by mixing peroxide of manganese into a paste with sulphuric acid, and heating it for some time to dull redness; oxygen is evolved, and the dry mass washed with water affords a solution of the sulphate of the protoxide, which may be crystallised by evaporation. This salt is much used in dyeing and calico-printing, for which purpose it is prepared by "igniting" peroxide of manganese mixed with about one-tenth its weight of pounded coal in a gas retort. A little HCl is added towards the end of the operation. The protoxide thus formed is dissolved in diluted sulphuric acid with the addition at the end of a little hydrochloric acid; the sulphate is evaporated to dryness, and again heated to redness in the gas retort; the iron is found, after the ignition, in the state of peroxide, and insoluble, the persulphate of iron being decomposed, while the sulphate of manganese is not injured by the temperature of ignition, and remains soluble. The solution is of an amethystine colour, and does not readily crystallise. When cloth is passed through sulphate of manganese and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it and rapidly becomes brown in the air; or it is at once peroxidised by passing the cloth through a solution of chloride of lime. The colour thus produced is called manganese brown (Graham).

Sulphate of manganese, as obtained by gentle evaporation from the neutral solution, forms rhombic prisms which contain 4 atoms of water. When the crystals are formed between 45° and 68° F. they contain 5 atoms of water, and are isomorphous with sulphate of copper; and when formed under 42° F. they include 7 atoms of water, and are isomorphous with sulphate of iron (Mitscherlich). And lastly, when a concentrated solution of sulphate of manganese is mixed with sulphuric acid, it yields on evaporation small granular crystals containing only 1 atom of water. The solubility of sulphate of manganese varies with its water of crystallisation; but, according to Brandes, the anhydrous salt is soluble in 2 parts of water at 60° F. and in its own weight at 122° F.; at a higher temperature its solubility diminishes. It is insoluble in alcohol. The taste of sulphate of manganese is styptic and bitterish, and the crystals have generally a slight tinge of pink. At 240° F. they lose 3 atoms of water, but retain 1 until heated above 400°; at a red-heat the salt becomes anhydrous, and in that state consists of the monohydrated salt $MnSO_4 + H_2O = 169$, which is greyish-white in colour, and is the starting-point of the manufacture of all manganese driers.

Manganese Acetate.—This salt is manufactured by double decomposition between acetate of lime and sulphate of manganese in equivalent proportions.

The reaction is as follows:—

$$\underset{\text{Calcium acetate}}{Ca(\bar{A})_2 +} \quad \underset{\text{Manganese sulphate}}{MnSO_4 =} \quad \underset{\text{Calcium sulphate}}{CaSO_4 +} \quad \underset{\text{Manganese acetate}}{Mn(\bar{A})_2.}$$

The brown acetate of lime may be used. A solution of acetate of manganese marking 22° Twaddell, specific gravity 1·110, is used in oil-boiling by steam in the proportion of 36 gallons to 10 tons of oil in conjunction with a small quantity of lead driers, the greater the proportion of which the darker is the resultant boiled oil (see Vincent's process of oil-boiling by steam, for which process this drier is especially applicable).

Hydrated Peroxide of Manganese.—Any sulphates or chlorides which may be present in small quantities are determined. If the hydrated oxide does not contain a large quantity of peroxide of manganese, it is worthless, and points to faulty washing. One or two per cents. of lime are harmless, larger quantities injurious. Besides the Mn content, the available oxygen is also determined.

		Mn.	Available O.	MnO_2.	Mn_2O_3.	MnO.	Oxides of Manganese.
Hydrated peroxide of manganese	A	38·11	10·14	49·37	10·43	—	59·80
Hydrated peroxide of manganese	B	53·67	10·87	33·33	46·82	—	80·15
Hydrated oxide of manganese	C	44·05	11·05	50·51	17·41	—	67·92
Hydrated oxide of manganese	D	51·31	8·59	12·23	62·60	—	74·83
Hydrated oxide of manganese	E	52·63	5·55	—	54·83	18·66	73·49
Hydrated protoxide of manganese	F	51·70	5·32	—	52·54	19·52	72·06

Manganese Borate.—This is prepared by precipitating a solution of 382 parts, i.e. one equivalent of borax, $Na_2B_4O_7 10aq.$, with 169 parts, i.e. one equivalent of the monohydrated sulphate of manganese, $MnSO_4, H_2O$. The sulphate of manganese should be free from iron and the borax from excess of alkali. The iron may be removed from the sulphate by roasting the sulphate and redissolving. If the chloride be used enough soda is added until the precipitate becomes white and the filtrate precipitated by borax. The excess of alkali may be neutralised by the addition of the requisite quantity of boracic acid. Precipitation should be effected in the cold. This substance, when pure and skilfully prepared, is a perfectly white powder, but whiteness is not a guarantee of purity, as it is often most grossly sophisticated with sulphate of lime, zinc oxide, etc. More samples contain lime either as borate or sulphate; a few per cents. does no harm if the borate is to be used for oil boiling. Where a high Mn content is indispensable a larger quantity is injurious. But such a drier may still be used for powdered siccatives where the drier mixed with a large bulk of inert matter is added direct to the paint. It is sometimes very unskilfully prepared. Some commercial samples submitted to J. G. McIntosh for analysis consisted of mere mechanical mixtures of sulphate of manganese and borax almost entirely destitute of drying power. Endemann and Paisley found the following percentages in four samples:—

1. Boric acid, 39·36; manganous oxide, 12·00
2. „ „ 40·18; „ „ 16·19
3. „ „ 37·38; „ „ 31·06
4. „ „ 11·09; „ „ 6·43

This salt is also made by acting on borax with manganous chloride and is supposed to be represented by the formula MnB_4O_7, but the washing with water to get rid of the sodium chloride partly decomposes it, and the salt is apt to turn brown from oxidation. Many manufacturers use a large excess of borax, and simply drain the precipitate without washing it. It often contains therefore 10 to 20 per cent. of sodium sulphate or sodium chloride. In the above analyses No. 3 was a washed product which had been bleached with sulphate of sodium. No. 4 contained rosin. When manganous sulphate is used in the manufacture of borate of manganese the yield is less than with the chloride, as the sodium sulphate dissolves the manganese borate. Weger found the Mn content to vary greatly, 22 per cent. of Mn being the highest in the white article. The composition is not MnB_4O_7 but more likely $2MnO . 3B_2O_3 . 3H_2O$. By reacting on manganous sulphate with the equivalent quantity of borax Endemann and Paisley obtained precipitates which, in two cases, contained 26·78 and 28·82 per cent. of manganous oxide and 42·36 and 39·69 per cent. of boric oxide (B_2O_3). If the salt were MnB_4O_7 the amounts of B_2O_3 for these two percentages of manganese should be 52·8 and 56·8 per cent. respectively. They recommend the following process for the manufacture of borate of manganese: Manganous chloride is precipitated with borax mixed with enough caustic soda to double the amount of soda present. The precipitate is washed twice with a little water. The loss of boric acid is found by analysing the wash water, and is replaced by mixing solid boric acid with the nearly dry precipitate, and drying the mixture thoroughly. It may then be regarded as MnB_4O_7, with either three or five molecules of water. Borate of manganese prepared in this way gave capital results as a drier.

Manganese Oxalate.—Manganese oxalate is made by precipitating a solution of oxalate of soda by a manganese salt. In boiling the oxalic acid of the manganese oxalate is decomposed with evolution of CO_2, etc. Very energetic oxidising properties are claimed for the residual manganese.

Glycerinated Borate of Manganese as a Drier.—H. Rutgers acts on the principle that manganese borate dissolves in glycerine, and less drier need be used when such a solution is added to linseed oil.

Manganese Nitrate.—Amongst other inorganic manganese salts the nitrate is the best; when added to hot linseed oil it decomposes with separation of an oxide, the gaseous particles of which convert the oil at 150° to 170° C. into a boiled oil.

The only organic acid salt of manganese used as a drier in actual practice is the acetate which is used in aqueous solution in oil boiling by steam, the high price of which is compensated by the small amount required.

Manganese Linoleate.—Manganese linoleate is made in the same way as lead linoleate. A linseed oil soft soap is precipitated by a solution of the monohydrated sulphate of manganese, 169 parts of which, or one equivalent, are equal to 112·2 parts, or two equivalents of pure caustic potash which contain 83·3 parts of anhydrous potassic oxide (the percentage of real alkali contained in pure caustic potash), and as 100 parts of linseed oil require 19½ parts of pure caustic potash for complete saponification, it is easy to make the necessary calculation when working with potash of any strength different from the pure, viz. 83·3 per cent. of real alkali. Or potash lye of a certain gravity may be kept in stock, and its richness in real alkali ascertained from the customary tables and the gravity as indicated by the hydrometer. For 100 lb. of linseed oil caustic potash equal to 16½ lb. of real alkali must be used, starting initially with a weak solution and finishing with a more concentrated. The soft soap of commerce contains about 50 per cent. of water, and though often made from linseed oil is not invariably so, and, moreover, it is grossly adulterated with starch, silicate of soda, and so on. The varnish-maker who makes his own driers should, therefore, make also his own soft soap. Manganese linoleate is precipitated, washed, pressed and dried in the same way as lead linoleate.

Rosinate of Manganese.—Rosinate of manganese is made in the same way as lead rosinate; for every 80 parts of pure caustic soda (containing 62 parts of pure anhydrous alkali sodium oxide) present in the solution of rosinate of soda, 169 parts of monohydrated sulphate of manganese are required for precipitation. Mixed rosinates of manganese and lead and mixed linoleates of manganese and lead, as well as mixed rosinates and linoleates of both lead and manganese, can easily be made in the wet way, e.g.: The latter mixed drier is made thus. Saponify equal weights of rosin and linseed oil and precipitate by a solution of a mixture of the acetates or nitrates of manganese and lead in molecular proportions, or the manganese salts may be precipitated by $MnSO_4$, and the mother liquor Na_2SO_4 filtered off and then the lead salts precipitated by $Pb(A)_2$. This complex product after fusion and solution in turps is a fine drier. It can of course after fusion be dissolved in linseed oil.

Fused rosinates and linoleates are made by dissolving the oxides of lead and manganese in rosin or in linseed oil respectively. The proportions may be calculated as follows: As the atomic weight of KHO 56·1 is to the saponification value of the rosin or linseed oil, say, 17·5 and 19·5 per cent. respectively, so is half the atomic weight of litharge 111·5 and manganese dioxide 43·5 to the amount of litharge or manganese required per cent. Commercial raw materials are often grossly adulterated.

Although the above is correct in theory, practice determines that rosin in a state of fusion is incapable of absorbing the above mentioned oxides sufficiently for total saturation of its acid content. Indeed, the working quantities are far below those of the theoretical figures, as the following must prove:—

TABLE SHOWING APPROXIMATE ABSORPTION BY ROSIN OF LEAD AND MANGANESE OXIDES.

Product.	Rosin, Parts by Weight.	Litharge, PbO, Parts by Weight.	Manganese, MnO_2, Parts by Weight.
Lead rosinate	100	12	—
Manganese rosinate . . .	100	—	5·6
Lead and manganese rosinate .	100	6	2

Rosinates of Manganese and Lead.—The true rosinates of manganese and lead are made not by saponifying rosin but by saponifying such hard resins as copal by caustic soda and reprecipitating by a salt of lead or manganese. They form interesting compounds, but they are even more intractable as far as solution in oil is concerned than the original resins (not rosin) from which they are derived.

In 1891 F. H. Thorpe determined the effect of temperature and of various driers on linseed oil during boiling.

He used Calcutta raw linseed oil. It was a very pale yellow colour, and cold pressed. In each experiment 50 c.c. was used, put into a tube of thin Bohemian glass, and plunged with several others into a sand-bath, the sand reaching half-way up the contents of the tube. During boiling the contents of the tubes were stirred. The drier, before being introduced into the oil, was rendered anhydrous. The best results were got by heating the sand-bath up to between 230° and 275° C. (446° to 527° F.). After heating, the quality of the oil was assessed by covering small plates of glass with it and allowing it to dry in a ventilated room. The varnish was considered dry when it could be touched without leaving finger-marks upon it. The table on p. 322 gives the results obtained. Some of them do not seem altogether in accordance with results obtained on the large scale. But results obtained by heating tubes in sand can hardly be regarded as comparative. Again, the influence of mass in oil boiling makes itself felt as in other chemical operations. Mere laboratory experiments can only serve as a rough guide.

Davidson in his report of what was practically a repetition of the above experiments in a copper dish claims, but in nowise proves, that he dissolved 2 per cent. each of litharge, red lead, and lead acetate in the oil in 20 minutes at 250° C., without finding any metallic residue, any metallic oxide residue, nor other insoluble! He gives no analysis of the boiled oils, and his statement, which flatly contradicts the practical experience of thousands of others, must be taken with more than the usual amount of reserve and caution for any credence to be given to Davidson's assertion. Lead driers leave a residue of metallic lead on the bottom of the pot.

The Manufacture of Rosinates and Linoleates.—The manufacture of metallic rosinate driers affords a good opportunity of showing

Siccative.	Quantity Employed (in Grammes).	Length of the Boiling (Hours).	Temperature (in Degrees C.).	Time taken to Dry (Hours).	Appearance of the Dry Coat.
Litharge	1·0	2¼	220	6	Almost colourless.
,,	0·2	2¼	250	10	,, ,,
,,	0·8	1½	250	10	,, ,,
Peroxide of lead	1·072	1½	220	several days	Strongly coloured.
Chloride ,,	1·274	2½	250-360	24	Slightly ,,
Red lead	1·024	2½	220-285	24	Strongly ,,
Oxalate of lead	1·323	2¼	300	did not dry	,, ,,
Tartrate ,,	1·6	2¼	270	24	,, ,,
Acetate ,,	1·46	2¼	270	12	Slightly ,,
Borate ,,	1·105	1½	220-300	20	,, ,,
Carbonate ,,	1·197	2	225	10	,, ,,
Oxide of zinc	0·5	2¼	250	45	Almost colourless.
Sulphate ,,	1·987	2½	285	45	,, ,,
,, ,,	1·5	2	230	45	Yellow.
Acetate ,,	1·0	2¼	235-280	40	Colourless.
Borate ,,	1·0	2	240	40	Almost colourless.
,, ,,	0·5	1½	240	46	,, ,,
,, ,,	0·5	1½	240	46	,, ,,
Citrate ,,	1·5	2½	230	36	,, ,,
Acetate of manganese	1·0	2¼	225-250	20	,, ,,
Borate ,,	1·625	2¼	220	20	Colourless and hard.
Sulphate ,,	1·72	2	240	40	,,
Oxalate ,,	1·64	2	230	40	,,
Acetate ,,	0·5	2	225-250	20	Strongly coloured.
Borate ,,	0·5	1	230	20	Colourless.
Acetate ,,	0·5	1¼	225-250	20	,,
Oxalate ,,	1·5	2½	230	36	,,
Sulphate ,,	1·5	2½	240	36	,,
Oxalate ,,	1·0	2¾	240	48	Yellow.
Citrate ,,	1·5	1½	230	24	Black.
Tartrate ,,	1·0	2½	230	24	Colourless.
Formiate ,,	1·0	1	200	24	Slightly coloured.

THE AMOUNT OF METALLIC OXIDE ACTUALLY DISSOLVED AND HELD IN SOLUTION PER CENT. BY CERTAIN OF (1) THE LEAD AND (2) THE MANGANESE BOILED OILS.

Drier.	Quantity of Drier.	Lead on Manganese per Cent.		
		Calculated.	Found.	
			I.	II.
Lead carbonate	1·197	2·030	1·392	1·477
,, acetate	1·466	2·230	1·396	1·338
Litharge	0·200	0·406	0·244	1·338
Lead borate	1·105	2·030	0·982	0·998
Manganese sulphate	1·720	1·870	0·045	0·038
,, borate	1·620	2·060	0·208	0·190
,, acetate	0·500	0·347	0·248	0·080
,, tartrate	1·500	0·670	0·049	0·043

the poor place taken by Germany in oil colour trade progress. In no department of chemical industry as in the oil and colour trade is the absolutely false idea so prevalent that we owe any great improvement to Germany and the Germans. All our knowledge about driers, their methods of manufacture, and the principle of their use has for several decades been credited to Germany, whereas the knowledge, if not our own, comes to us direct from France. Germany has not made one single improvement in the industry since or before it became an Empire—since or before 1870. Chevreul, a Frenchman, Jean, another Frenchman, and Barruel, another Frenchman, and Zinckowicz, evidently a Polish refugee living in Paris, all knew as much or more about driers and their catalytic actions and functions than any German does at the present day. Jean and Barruel and Zinckowicz were experts in the use of borate of manganese. So also was our own Vincent, who boiled oil by steam in Milford Lane, Strand, prior to 1870 with a manganese cum lead drier.

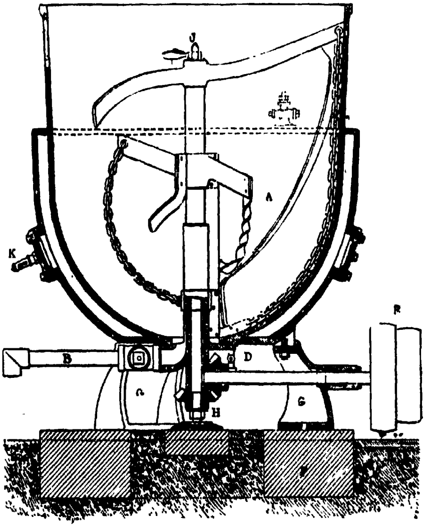

FIG. 81.—Steam-jacketed pan for use in making rosinate of soda, rosin soap, and fitted with revolving chain agitator.

All German books on oils are conspicuously silent on the fact that both rosinate and borate driers originated in France, and were the invention of the Polish refugee Zinckowicz. Be it well understood that this Zinckowicz made borates, benzoates, and urobenzoates (hippurates) of not only manganese, but also of nickel and cobalt.

The renaissance of cobalt driers, half a century after Zinckowicz, was hailed as the advent of new and hitherto unknown driers, and again put down to the Germans!

Benzoate of Cobalt. Zinckowicz's Method of Preparation.—Benzoic acid is dissolved in boiling water, and the stirred liquor is gradually mixed with powdered cobalt carbonate until all effervescence ceases, and blue litmus does not turn red in the liquor. The excess of carbonate is separated by filtration, the liquor is evaporated to dryness, and the heating is continued until the salt has lost all its water and has become of a light brown colour. Zinckowicz evidently knew that *hydrated organic driers do not dissolve in oil.* The salt thus prepared is an amorphous hard and brownish material, which may be powdered like rosin, and which may be kept in the pulverulent state in any climate simply folded in paper. The Mn drier presents nearly the same physical characteristics as the cobalt salt; applied under the same conditions, it dries a little more rapidly and a little less is needed. The benzoate of manganese is prepared in the same manner by substituting $MnCO_3$ for $CoCO_3$. An experiment by Zinckowicz with this drier showed that in the ratio of 3 lb. to 1000 lb. of linseed oil mixed with about 1200 lb. of zinc white, a piece of painting was dried in from 18 to 20 hours. The temperature was relatively cold and wet and between 12° and 15° C.

Cobalt Borate.—A soluble salt of cobalt; the sulphate, for instance, is dissolved in cold water, and this solution is precipitated by a cold one of borax. The precipitated borate of cobalt is collected on cloth filters, washed with cold water, and dried in the air.

The chief, if not the only acid existing in common rosin, is a dibasic acid which has been termed sylvic, pimaric, and abietic acid, and different observers have ascribed to it different formulæ and different molecular weights. Mach gave it the formula $C_{19}H_{28}O_2$, with the molecular weight of 288. On the other hand, Fahrion named what he claims to be the same acid, sylvic acid, with the formula $C_{20}H_{30}O_2$, with the molecular weight 302. As the acid of rosin is dibasic, i.e. its displaceable hydrogen requires 2 atoms of a monad metal to replace it, it follows that 112·2 parts of KHO are required to saturate 1 molecule of the free acid in rosin. But there are other substances in rosin besides its free acid, which consume potash before complete saponification occurs, viz. rosin ethers. So the saponification number of rosin is always higher than its acid number.

Manufacture of Rosinates.—The first stage in the manufacture of rosinates is the manufacture of rosinate of soda, and if too little or too much alkali be used to saponify the rosin, the soluble drier made from such rosinate of soda will be liable to contain free rosin on the one hand, or an excess of base on the other. When carbonate of soda is used in excess, the carbonate of the metals forming the rosinates or linoleates is precipitated on to the rosinate or linoleate. As the precipitated carbonates of lead and manganese are both energetic driers, possibly little harm is done by a slight excess. When caustic soda is used, any excess of the latter combines with the metal of the precipitating salt to form a hydrate, and here again little, if any, injury is caused to the resultant drier. The first thing to do, therefore, is to determine the saponification value as described elsewhere.

COMBINING WEIGHT OF DIFFERENT SAMPLES OF AMERICAN ROSIN. (EVANS AND BEACH.)

No.	Grade.	Combining Weight.	No.	Grade.	Combining Weight.
1	W. G.	328·9	9	K.	355·6
2	F.	333·5	10	I.	355·9
3	M.	334·5	11	H.	354·6
4	N.	351·4	12	G.	354·9
5	W. W.	339·9	13	F.	336·8
6	W. G.	344·5	14	E.	347·9
7	N.	347·5	15	D.	346·9
8	M.	339·8	16	C.	350·3

Evans and Beach found that the combining weight of rosin varies widely in both directions from that given by Twitchell, and what is more disappointing is that the grade, which is largely determined by the colour, has little or no relation to the combining weight.

The molecular weight of sylvic acid with the formula $C_{20}H_{30}O_2$ is

C 20 × 12	240
H 30 × 1	30
O_2	32
	302

In determining saponification values of both rosin and linseed oil cheese-paring calculations are absurd and shall not be indulged in here. The same remark applies to the saponification of linseed oil The following table of alkali required to saponify oils of a mean molecular weight is calculated to the second decimal place of a litre for as much as 10 metric tons of oil:—

	Litres of Caustic Alkali, Sp. Gr. 1·1.		Litres of Caustic Alkali, Sp. Gr. 1·2.		Litres of Caustic Alkali, Sp. Gr. 1·3.		Litres of Caustic Alkali, Sp. Gr. 1·355.	
	NaHO.	KHO.	NaHO.	KHO.	NaHO.	KHO.	NaHO.	KHO.
1000	1461·40	1482·56	658·06	742·81	397·54	485·13	319·11	403·54
2000	2922·81	2965·12	1316·12	1449·61	795·07	970·27	628·23	807·0
3000	4384·21	4447·67	1974·18	2174·42	1192·61	1455·40	957·34	1210·61
4000	5845·62	5930·23	2632·24	2899·22	1590·14	1940·53	1276·45	1614·1
5000	7307·02	7412·79	3290·30	3624·03	1987·68	2425·67	1595·57	2017·6
6000	8768·42	8895·35	3948·35	4348·84	2385·21	2910·80	1914·68	2421·2
7000	10229·83	10377·91	4606·41	5073·64	2782·75	3395·93	2233·79	2824·7
8000	11691·23	11860·46	5264·47	5798·45	3190·28	3881·06	2552·90	3228·3
9000	13152·64	13343·02	5922·53	6523·25	3577·82	4366·20	2872·02	3631·8
10000	14614·04	14825·58	6580·59	7248·06	3975·35	4851·33	3191·13	4035·3

STRENGTH OF SOLUTIONS OF CAUSTIC POTASH ACCORDING TO BAUMÉ'S HYDROMETER, WITH EQUIVALENT READING ON TWADDELL'S SCALE.

Density.	Baumé °.	Twaddel °.	100 Lb. Contain in Lb.	100 Lb. Contain in Lb.	100 Gallons Contain in Lb.	100 Gallons Contain in Lb.
			K_2O.	KOH.	K_2O.	KOH.
1·007	1	1·4	0·7	0·9	7	9
1·014	2	2·8	1·4	1·7	14	17
1·022	3	4·4	2·2	2·6	22	26
1·029	4	5·8	2·9	3·5	30	36
1·037	5	7·4	3·8	4·5	39	46
1·045	6	9·0	4·7	5·6	49	58
1·052	7	10·4	5·4	6·4	57	67
1·060	8	12·0	6·2	7·4	66	78
1·067	9	13·4	6·9	8·2	74	88
1·075	10	15·0	7·7	9·2	83	99
1·083	11	16·6	8·5	10·1	92	109
1·091	12	18·2	9·2	10·9	100	119
1·100	13	20·0	10·1	12·0	111	132
1·108	14	21·6	10·8	12·9	119	143
1·116	15	23·2	11·6	13·8	129	153
1·125	16	25·0	12·4	14·8	140	167
1·134	17	26·8	13·2	15·7	150	178
1·142	18	28·4	13·9	16·5	159	188
1·152	19	30·4	14·8	17·6	170	203
1·162	20	32·4	15·6	18·6	181	216
1·171	21	34·2	16·4	19·5	192	228
1·180	22	36·0	17·2	20·5	203	242
1·190	23	38·0	18·0	21·4	214	255
1·200	24	40·0	18·8	22·4	226	269
1·210	25	42·0	19·6	23·3	237	282
1·220	26	44·0	20·3	24·2	248	295
1·231	27	46·2	21·1	25·1	260	309
1·241	28	48·2	21·9	26·1	272	324
1·252	29	50·4	22·7	27·0	284	338
1·263	30	52·6	23·5	28·0	297	353
1·274	31	54·8	24·2	28·9	308	368
1·285	32	57·0	25·0	29·8	321	385
1·297	33	59·4	25·8	30·7	335	398
1·308	34	61·6	26·7	31·8	349	416
1·320	35	64·0	27·5	32·7	363	432
1·332	36	66·4	28·3	33·7	377	449
1·345	37	69·0	29·3	34·9	394	469
1·357	38	71·4	30·2	35·9	410	487
1·370	39	74·0	31·0	36·9	425	506
1·383	40	76·6	31·8	37·8	440	522
1·397	41	79·4	32·7	38·9	457	543
1·410	42	82·0	33·5	39·9	472	563
1·424	43	84·8	34·4	40·9	490	582
1·438	44	87·6	35·4	42·1	509	605
1·453	45	90·6	36·5	43·4	530	631
1·468	46	93·6	37·5	44·6	549	655
1·483	47	96·6	38·5	45·8	571	679
1·498	48	99·6	39·6	47·1	593	706
1·514	49	102·8	40·6	48·3	615	731
1·530	50	106·0	41·5	49·4	635	756
1·546	51	109·2	42·5	50·6	655	779
1·563	52	112·6	43·6	51·9	681	811
1·580	53	116·0	44·7	53·2	706	840
1·597	54	119·4	45·8	54·5	731	870
1·615	55	123·0	47·0	55·9	754	902
1·634	56	126·8	48·3	57·5	789	940

It only aggravates matters when these cheese-paring calculations are the work of a man who prides himself on being an eminent scientist—which shows that one may take a scientific man as a guide and still in reality be in actual practice a rule-of-thumb man of the very worst type, vainly imagining he is working scientifically. The only object of such a table could be to impress the rule-of-thumb man with the wonderful accuracy of the man of science who can calculate to the second decimal place of a litre the number of litres required to saponify 10 tons of oil. If the saponification value of the oil in question was known, such fastidious accuracy might be excusable; here it is most grotesque.

The strength of commercial alkali is always expressed in per cent. of anhydrous alkali, as in the second horizontal line; if the caustic potash be pure it contains 94·2 per cent., and knowing the saponification value of the oil and the percentage of anhydrous potash in the alkali being used, the calculation of the amount required to saponify any given oil or rosin whose saponification value is known is a simple matter. Thus 100 lb. of rosin will, with the saponification value of 170, require 17 lb. of potash KHO, the nearest solution, using 100 lb. of that strength, specific gravity 1·147, say about 29° Tw. The figures are for pure potash. The best plan of course would be to dissolve the 17 lb. of potash in water and make up to a given strength, say 10 per cent. or 12 per cent. KOH. Such a solution, 12 per cent., as will be seen from the table, has a specific gravity of 1·100, 20° Tw., and 10 gallons of it contain 11·9 lb. of KOH, 15 gallons of it contain nearly 18 lb.; the right proportion is about 14½ gallons.

THE MANUFACTURE OF METALLIC LINOLEATES AND OTHER METALLIC SOAPS.

Aluminium Linoleate.—This is one of the most important of all. Alumina itself is capable of saponifying fats, but the aluminates of potash or soda do so strongly, and produce a light aluminium soap which has many uses, in waterproofing wood and garments for example, and in paper manufacture.

Lead Linoleate.—This is made by saponifying drying oils, chiefly those of linseed and hemp oils, with red lead, litharge or white lead, or by precipitating a solution of ordinary soap with lead acetate. It is used as a siccative.

Lead acetate, $Pb(C_2H_3O_2)_2 3H_2O$. 3·5 lb. would decompose 7·7 lb. of soap.

Magnesium Linoleate.—This soap has of late assumed considerable importance in candle manufacture. Now that the price of magnesia has fallen, its advantages over lime as a saponifying agent can be taken advantage of. Less of it is required than of lime for any given quantity of fat, and the magnesium sulphate formed when the soap is decomposed with sulphuric acid is soluble. The fatty acids

STRENGTH OF SOLUTIONS OF CAUSTIC SODA AS DETERMINED BY BAUMÉ'S HYDROMETER, WITH THE EQUIVALENT READING ON TWADDELL'S SCALE.

Density.	Baumé.	Twaddell.	Per Cent. Na_2O.	Per Cent. NaOH.	One Cubic Metre Contains in Kg or 100 Gallons in Lb.	One Cubic Metre Contains in Kg or 100 Gallons in Lb.
					Na_2O.	NaOH.
1·007	1	1·4	0·47	0·61	4	6
1·014	2	2·8	0·93	1·20	9	12
1·022	3	4·4	1·55	2·00	16	21
1·029	4	5·8	2·10	2·71	22	28
1·036	5	7·2	2·60	3·35	27	35
1·045	6	9·0	3·10	4·00	32	42
1·052	7	10·4	3·60	4·64	38	49
1·060	8	12·0	4·10	5·29	43	56
1·067	9	13·4	4·55	5·87	49	63
1·075	10	15·0	5·08	6·55	55	70
1·083	11	16·6	5·67	7·31	61	79
1·091	12	18·2	6·20	8·00	68	87
1·100	13	20·0	6·73	8·68	74	95
1·108	14	21·6	7·30	9·42	81	104
1·116	15	23·2	7·80	10·06	87	112
1·125	16	25·0	8·50	10·97	96	123
1·134	17	26·8	9·18	11·84	104	134
1·142	18	28·4	9·80	12·64	112	144
1·152	19	30·4	10·50	13·55	121	156
1·162	20	32·4	11·14	14·37	129	167
1·171	21	34·2	11·73	15·13	137	177
1·180	22	36·0	12·33	15·91	146	188
1·190	23	38·0	13·00	16·77	155	200
1·200	24	40·0	13·70	17·67	164	212
1·210	25	42·0	14·40	18·58	174	225
1·220	26	44·0	15·18	19·58	185	239
1·231	27	46·2	15·96	20·59	196	253
1·241	28	48·2	16·76	21·42	208	266
1·252	29	50·4	17·55	22·64	220	283
1·263	30	52·6	18·35	23·67	232	299
1·274	31	54·8	19·23	24·81	245	316
1·285	32	57·0	20·00	25·80	257	332
1·297	33	59·4	20·80	26·83	270	348
1·308	34	61·6	21·55	27·80	282	364
1·320	35	64·0	22·35	28·83	295	381
1·332	36	66·4	23·20	29·93	309	399
1·345	37	69·0	24·20	31·22	326	420
1·357	38	71·4	25·17	32·47	342	441
1·370	39	74·0	26·12	33·69	359	462
1·383	40	76·6	27·10	34·96	375	483
1·397	41	79·4	28·10	36·25	392	506
1·410	42	82·0	29·05	37·47	410	528
1·424	43	84·8	30·08	38·80	428	553
1·438	44	87·6	31·00	39·99	446	575
1·453	45	90·6	32·10	41·41	466	602
1·468	46	93·6	33·20	42·83	487	629
1·483	47	96·6	34·40	44·38	510	658
1·498	48	99·6	35·70	46·15	535	691
1·514	49	102·8	36·90	47·60	559	721
1·530	50	106·0	38·00	49·02	581	750

For notes, see opposite page.

swim on the top of the solution of it, and are more easily separated from it than from the insoluble calcium sulphate.

Manganese sulphate, $MnSO_4 7H_2O$. 2·5 lb. would decompose 7·7 lb. of soap.

Manganese Linoleate.—An important drier made by precipitating a solution of linseed oil soap with one of a manganese salt, or by dissolving sulphate or black oxide of manganese in linoleic acid, linseed oil, hemp oil, etc., by the aid of heat.

Tin Linoleate.—This is made by precipitating linseed oil soap solution with one of stannous or stannic chloride.

The colours of the various insoluble linoleates are as follows :—

Calcium soap	white
Copper „	green
Zinc „	white
Lead „	„
Manganese soap	pale pink
Aluminium „	white
Ferric soap	yellow

A peculiar property of the linoleates insoluble in water is that they are freely soluble in turpentine, benzine, light petroleum, and carbon bisulphide, while the palmitates and stearates are insoluble; hence the insoluble soaps produced from a soap made from olive oil (consisting principally of sodium oleate) can be dissolved almost entirely, whereas the soaps made from palm oil (consisting largely of sodium palmitate) or tallow (consisting largely of sodium stearate and palmitate) only dissolve very slightly, that portion which dissolves being the linoleate of the metal, there being some linoleic acid also contained in these soaps.

Use is made of this fact in applying a solution of one of these metallic linoleates in benzine, or petroleum spirit, for waterproofing paper, cotton, and leather.

Potash and soda soaps, soluble in water and giving a solution which removes grease, have long been employed as cleansing agents; other soaps are, however, not so well known, though they are extremely useful. It is a well-known fact that a soap results from the combination of a fatty acid with a base; in the case of the soluble soaps, the

Notes for Table on p. 328.

1. To convert per cents. K_2O into their equivalents of Na_2O, multiply by 62 and divide by 94.

2. To convert per cents. KOH into their equivalent in NaOH, multiply by 40 and divide by 56·1.

3. To convert per cents. Na_2O into their equivalents of K_2O, multiply by 94 and divide by 62.

4. To convert per cents. NaOH into their equivalents in KOH, multiply by 56·1 and divide by 40.

A smaller amount of NaOH = 40 or Na_2O = 62 will neutralise the same amount of acid as the larger quantities of K_2O = 94·2 or KHO = 56·1. Hence inverse proportion in 1 and 2 and ordinary proportion in 3 and 4.

base is either potash or soda, but the soaps formed by the union of a fatty acid with the metals calcium, barium, magnesium, aluminium, iron, copper, etc., are all insoluble in water. The oils and fats used in the preparation of soaps are never pure glycerides; hence the soaps contain more than one fatty acid, the three fatty acids oleic, palmitic, and stearic usually occurring together. The soaps of commerce are, therefore, mixtures of potassium or sodium oleate, palmitate, and stearate, the formulæ for which are given below:—

	Oleic.	Palmitic.	Stearic.
Acid	$HC_{18}H_{33}O_2$	$HC_{16}H_{31}O_2$	$HC_{18}H_{35}O_2$
Sodium salt	$NaC_{18}H_{33}O_2$	$NaC_{16}H_{31}O_2$	$NaC_{18}H_{35}O_2$
Potassium salt . . .	$KC_{18}H_{33}O_2$	$KC_{16}H_{31}O_2$	$KC_{18}H_{35}O_2$

In washing with hard water it will be easily noticed that a large quantity of soap is used up before a lather is obtained, and that, subsequently, a white curdy deposit is formed; this is a lime soap insoluble in water, and it is produced by the union of the fatty acids of the soap with the lime present in the water. The same reaction may be brought about by the addition of a solution of calcium chloride to a solution of soap, the curdy precipitate falling as the two are mixed until, when the calcium chloride is in excess, a lather ceases to be produced when the liquid is agitated. This is the general method of preparing the insoluble soaps, though other methods are practised on a large scale for particular purposes.

The double decomposition which occurs when a solution of a soap is precipitated with a solution of calcium chloride is shown in the following equation, the soap being represented as sodium oleate:—

$$2NaC_{18}H_{33}O_2 + CaCl_2 = Ca(C_{18}H_{33}O_2)_2 + 2NaCl.$$

It will be seen that one molecule of calcium chloride will decompose two molecules of sodium oleate, and, knowing the weights of these molecules, it is easy to calculate what any given weight of a soap will require of calcium chloride to decompose it, so that in the actual work none of the reagents may be thrown away.

For instance, two molecules of sodium oleate weighing 608 are decomposed by one molecule of calcium chloride weighing 111, or 5·5 pts. of sodium oleate are decomposed by 1 pt. of calcium chloride.

The molecular weights of sodium stearate and sodium palmitate are nearly the same as that of sodium oleate; that is, two molecules of the first equal 612 and two molecules of the second equal 576; therefore an ordinary soap containing all three acids may be assumed to have a molecular weight intermediate to these, and two molecules would equal approximately 600; one part of calcium chloride would therefore decompose 5·4 pts. of such a soap.

The above calculation assumes that the soap is pure and dry, which, of course, is not the case, but with a soap containing 30 per cent. of water,

$$5{\cdot}4 \times \frac{100}{70} = 7{\cdot}7 \text{ lb.}$$

would be decomposed by 1 lb. of calcium chloride.

Lime Soap.—Lime soap has been of great importance in the candle trade since Milly succeeded in replacing the costly process of saponifying fats with caustic soda lye by the cheaper method of using lime. The resulting insoluble lime soap is decomposed with dilute sulphuric acid. When the calcium sulphate formed has settled to the bottom, the fatty acids are run off and allowed to cool. The solid ones among them are made into candles. The precipitation of lime soap which occurs when ordinary soap is used with hard water is well known.

The reaction which takes place when any other metallic salt is employed is precisely similar, and the calculated quantities of the following salts would decompose the same weight of soap:—

Copper sulphate, $CuSO_45H_2O$. 2·2 lb. would decompose 7·7 lb. of soap.

Copper Soap.—This is prepared by precipitating a solution of a hard or soft ordinary soap with one of sulphate of copper or by boiling oleic acid with copper carbonate. It is a green soap, which dries to a brittle mass, slightly soluble in alcohol but freely in oils or in ether.

Copper Stearate. 75 lb. of stearine are melted in a copper kettle and 13 lb. of sodium or potassium hydrate, made up to 18 per cent. solution, run slowly in and stirred until the soap is quite clear. In another tub 57 lb. of copper sulphate are dissolved and the stearine soap thrown out with this solution. The copper stearate formed is removed to another pan, and the water driven off when it is packed in wooden casks.

Zinc sulphate, $ZnSO_47H_2O$. 2·6 lb. would decompose 7·7 lb. of soap.

Zinc Soap.—This is a plate-like mass of yellowish-white and is prepared by heating zinc oxide with a fat or oil, or by precipitating ordinary soap with a zinc salt. It is used with zinc white in painting.

Ferrous sulphate, $FeSO_47H_2O$. 2·5 lb. would decompose 7·7 lb. of soap.

Iron Soap.—Prepared by precipitating a solution of ordinary soap with one of ferrous sulphate. A mixture of copper soap and iron soap is used to give plaster casts a very durable bronze.

Aluminium and ferric salts decompose six molecules of soap as shown in the following equation:—

$$6NaC_{18}H_{33}O_2 + Al_2(SO_4)_3 = Al_2(C_{18}H_{33}O_2)_6 + 3Na_2SO_4,$$

therefore:—

Aluminium sulphate, $Al_2(SO_4)_318H_2O$. 4·0 lb. would decompose 7·7 lb. of soap.

Alum, $Al_2(SO_4)_3K_2SO_424H_2O$. 5·7 lb. would decompose 7·7 lb. of soap.

The choice of paints for painting the bottom of ships, namely, from the water-line downwards, is of importance, as much is required of such paints. It is well known that in a short time numbers of small sea animals attach themselves to the bottom of sea-going vessels, and sometimes form a considerable crust, which influences their speed in a marked degree, both by the additional weight and the greater friction thereby occasioned. The object therefore of paints for this purpose is to produce a poisonous effect upon these sea animals, to prevent them accumulating. Various means have been tried; for instance, the addition of Schweinfurt green to ordinary oil paints. This has a certain effect, but in the first place the grinding of the arsenical green with varnish has a bad effect upon the health of workmen, and, further, the paint after completely drying, no longer affects the small sea animals in a sufficient degree in order to kill them. Paints have also been prepared which do not dry completely, so as to have a stronger action; these are generally applied hot, but a paint that becomes quite hard is probably to be preferred.

Paints for the bottoms of ships should also give a good durable coating, as repainting below the water-line is costly and troublesome. Compounds of metals with fatty acids constitute the chief components, according to the following processes, for good paints. In the first place two metal compounds are prepared, copper linoleate and copper stearate; the latter for use in paints which are to remain soft, and which must be applied hot. A further copper compound is also required to act as the poisonous principle, such as verdigris.

Copper linoleate.—An 18 per cent. solution is made from 18 lb. of caustic potash or caustic soda and heated in a kettle to 70° C. (158° F.); 90 lb. of linseed oil are then slowly run in with constant stirring; the whole is then diluted with 5 gallons of water, and heated up until the soap boils clear. In a suitable cask, 55 lb. of copper sulphate are dissolved in 50 gallons of water, and slowly precipitated while well stirring with the linseed oil soap; after settling out, the liquor is drawn off and the precipitate of copper linoleate well washed and strained; it is then brought into a cast-iron kettle and heated to 100° C. (212° F.) to drive off the remaining water, being afterwards packed in wooden casks. The yield on the above given quantities is about 95 lb.

Verdigris.—It has been recommended to make verdigris by double decomposition. 60 lb. of lead acetate, after melting in a copper kettle, are poured into a flat copper pan, and 40 lb. of finely powdered copper sulphate stirred in. A tough paste forms which is allowed to cool when it has become quite uniform, and after drying it is ground in a closed mill. For this latter operation it is recommended that workmen should use good respirators, as verdigris is very poisonous. If it be so it is from the presence of lead incidental to this method. Workmen in ordinary verdigris are at any rate immune. But this extemporaneous method may very well yield a poisonous product.

Anti-Fouling Paints.—Paints suitable for painting the bottom of ships are made by mixing the above metal compounds in various proportions with lithopone or zinc white and heavy spar, and grinding the mixture with a good oil varnish. If the paint is desired to dry hard, salt solution is added.

As examples, a hard drying paint is obtained by taking 30 lb. copper linoleate, 25 lb. lithopone, 10 lb. barytes, 30 lb. oil varnish; or 30 lb. copper linoleate, 15 lb. zinc white, 10 lb. lithopone, 30 lb. oil varnish, 5 lb. rosin solution; or 25 lb. copper linoleate, 25 lb. verdigris, 10 lb. white lead, 10 lb. barytes, 30 lb. oil varnish; or 25 lb. copper linoleate, 35 lb. verdigris, 30 lb. oil varnish, 3 lb. salt solution. And for a paint that remains soft: 25 lb. copper linoleate, 15 lb. copper stearate, 15 lb. lithopone, 20 lb. oil varnish; or 30 lb. copper linoleate; 10 lb. copper stearate, 10 lb. lithopone, 5 lb. verdigris, 15 lb. oil varnish; or 25 lb. copper linoleate, 15 lb. verdigris, 15 lb. copper stearate, 5 lb. lithopone, 12 lb. oil varnish, and so on. By varying the proportions a harder or softer drying paint can be obtained, and also more or less poisonous according to the amount of verdigris used.

It may be mentioned that good results have been obtained with the given mixtures in small trials, the essentials being the metal compounds with fatty acids; doubtless therefore the same results will be obtained in the large scale.

Waterproofing of Fabrics.—There is another method of waterproofing with insoluble soaps, the fabric to be treated being first passed through a solution of soap, then through a solution of alum, zinc sulphate, or copper sulphate, whereby an insoluble soap of one of these metals is precipitated within and upon the fibres, and, not being easily wetted with water, it forms a very efficient weatherproof material. Canvas for sailcloth and for tent-making is treated in this way, and, while the fabric is very little altered in appearance, the deposit of insoluble soap prevents the wetting of the fibres, and therefore keeps the moisture out. The fabrics treated with a copper soap in the above way are also rot proof, owing to the protection afforded by the copper compound. In this method of operating, it is of very little importance what kind of soap is employed for common fabrics, a common yellow soap or soft soap being equally suitable; for fine white canvas a pure white soap is, of course, the best to use.

If a solution of soft soap be made and an aniline dye added, a solution of manganese chloride, calcium chloride, zinc chloride, or alum throws down a precipitate of an insoluble soap, which combines more or less with the colouring matter. Basic dyes, such as magenta or Bismarck brown, are best for this purpose, but several other dyes have been tried and found to give a similar result.

Magenta yields maroon-coloured precipitates.
Bismarck brown yields buff-coloured precipitates.
Aniline red yields red-coloured precipitates.
Phloxine yields scarlet-coloured precipitates.
Erythrosine yields scarlet-coloured precipitates.
Extra Ponceau yields deep red-coloured precipitates.
Chrysoidine yields deep orange-red coloured precipitates.
Aniline cotton orange yields deep orange-coloured precipitates.
Logwood extract yields violet-coloured precipitates.

These precipitates, after drying, are all soluble in carbon bisulphide, benzene, and petroleum; freely so in the two first named, but more sparingly in the latter.

The coloured oleates formed in the above manner are suitable for use in staining and waterproofing fabrics, and for a variety of other purposes where colours soluble in oils are desired, for instance, in colouring waxes and oils.

Basic dyes added to a solution of soft soap and then precipitated by the addition of acetic acid yield coloured pasty precipitates, consisting of the colour base probably combined with oleic acid. The precipitates produced by this method are very brilliantly coloured, and, if the acetic acid is used only in slight excess, very little of the colour is left in the liquid. The dyes produced in this manner are insoluble in water, but freely soluble in benzene and the other solvents. For colouring oils and waxes they leave nothing to be desired.

Soluble Driers.—The origin of terebene was well known to Mulder, as he advises the oil to be heated with a known quantity of litharge and pyrolusite, and a known weight of the resultant product to be added to the oil, to hasten its drying. This is the formation or principle on which terebene is based, by dissolving the crude mixed linoleate so obtained in turps. Later on, Binks heated oil with excess of litharge, and mixed the lead soap so obtained, to the extent of 0·2 to 0·5 per cent. with linseed oil. Owing to the formation of a large proportion of oxyacids, linoleate of lead, made by heating linseed oil with litharge, does not dissolve in petroleum spirit. Mulder explained that the oil was first converted into a lead linoleate, and that on adding this linoleate to the untreated hot oil, it dissolved therein. The lead and manganese salts of linoleic acid (linoleates), and of abietic acid (rosinates), have been generally used in oil-boiling and varnish-making. They can be dissolved in oil at a low temperature, or their solution in turps or other solvent is added to the varnish or oil to be treated. They were sold in the early eighties of last century, and found a very ready market. Besides linoleates and rosinates, oleates were also sold. Lead oleate was first used by Bouis, also palmitates, but these are seldom or never used. Ch. Van Zoul treates the mixed fatty acids of linseed oil in alkaline solution by Hazura's method, with permanganate, and converts the mixture of hydrolysed fatty acids into manganese salts for use as driers. Soluble rosinates and other organic salts of cobalt and manganese were made and patented away back in the sixties or seventies of last century for use as driers. Soluble driers are divided into (1) fused and (2) precipitated linoleates and (3) fused and (4) precipitated rosinates. (1) The fused driers are made by fusing the acids and bases together; (2) the precipitated driers are made by precipitating a solution of the sodium salt of linoleic acid, or abietic acid with an aqueous solution of a Pb or Mn salt. The fused driers are sold as more or less dark coloured lumps, or ground. Precipitated driers are less ponderous, and are pure white or slightly tinted in colour. But this light colour is due to their being hydrated compounds. Manganese browns on keeping and manganese linoleate is soft and pasty, and it blackens as it ages. The use of soluble driers is very easy. Linseed oil is heated to 120° to 150° C. (248° to 302° F.), and 1 to 3 per cent. of the drier dissolved therein without residue, or 1 part of drier is dissolved in 2 of linseed oil, and mixed with a certain quantity of untreated linseed oil. Soluble driers, moreover, especially when previously fused, dissolve in turps, and their solution in turps in the proportion of 1 to 2 or 2 to 3 are sold as liquid driers, but precipitated driers do not dissolve until all combined water is expelled by heat. Precipitated driers must therefore be fused before solution in oil or solvents. The extensive use of soluble driers in the U.S.A. has given rise to the term "boiling oil through the bunghole," and "bunghole oil". So far back as 1890 the old driers were largely supplanted by soluble driers.[1]

Soluble Driers, Constitution.—The preparation of fused linoleates and rosinates, the combination of the metallic oxides with the acids, and the saponification of the esters are operations of a somewhat complex nature, and an increase of temperature may lead to decomposition, and, in the case of manganese, oxidation; again, it is sometimes difficult to say in which of its forms the manganese is present, so that we never know whether we are dealing with a manganous or a manganic salt. These drawbacks disappear in dealing with precipitated driers, but here there is a possibility of basic salts being formed.

Weger fixes the normal constitution of the four compounds—manganese rosinate, lead manganese rosinate, manganese linoleate, and the lead manganese salt of the same acid—used as soluble dryers (the soluble salts of lead alone being but little employed) as 3·2 per cent. of soluble manganese in fused manganic rosinate, 6 (rarely as much as 7) per cent. in precipitated manganous rosinate, and 9 to 9·5 per cent. in good fused manganese linoleate. A few instances have occurred when the proportion reached 11 per cent., indicating either a more extensive dissociation of the acids in the linseed oil or the formation of basic salts.

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[1] It was about that time that the syndicate working Hartley and Blenkinsop's process wanted £100,000 for the Russian rights.

Weger found 30 per cent. of soluble lead in a fused lead linoleate. He explains this by assuming that the residual glycerine had combined with the excess of Pb. Calculating soluble Pb and Mn as manganese and lead linoleates or rosinates is complicated and difficult. First the saponification number of the linseed oil, also the neutralisation number of the fatty acids, linoleic acid, and abietic acid vary widely. Average figures must be taken :—

Saponification number of linseed oil	190
Neutralisation " " " fatty acids	198
" " " rosin	170

Calculating from these figures we get :—

	Percentage of Mn or Pb.
Manganese linoleate	8·9 Mn.
Manganic "	6·1 "
Manganous rosinate	7·7 "
Manganic "	5·3 "
Lead linoleate	26·9 Pb.
" rosinate	24·0 "

Weger found in fused Pb Mn rosinate, 9·90 soluble Pb (no insoluble Pb), 1·4 per cent. soluble Mn, 0·10 insoluble Mn, which was calculated to 41·0 per cent. lead rosinate, 27 per cent. manganic rosinate, and 30 to 35 per cent. free rosin. Sophistication with free rosin cannot do much damage in the sequel, as only 23 per cent. of drier is added to the oil, so that the free rosin in the boiled oil is only small. Free rosin increases the solubility.

The following desirable specifications have been enunciated. Some are impracticable: (1) The drier should darken the oil very little if at all. (2) The drier should cause no turbidity in fatty acid and mucilage-free oil. (3) The oil containing the drier should dry rapidly, in 12 hours at least, but better in 8 hours or less. (4) The drier must be cheap.

An ideal siccative conforming in every particular to all four specifications is not to be had. As to points (1) and (2) soluble driers are superior to insoluble driers. As to (3) soluble driers dry more rapidly than insoluble driers. As to (4) oil-boiling means fuel, time, and labour, and with linseed oil at £60 per ton, rosin at £50, and turps over £100 per ton, cheap driers are for the time as dead as the dodo. But it must be remarked here once more that rosin free or combined in linseed oil, if raw or boiled, is an absolutely illegal addition.

The following recipes for American Japans, driers, and varnish enamel vehicles are from an American source. The British reader will do well to remember that the American gallon is ⅙ less than a British imperial gallon :—

1. GRINDING JAPAN.

30 gallons Calcutta oil.
100 lb. X, XX, or XXX kauri gum, No. 3.

Melt the gum, boil the oil to 500° F., and mix. Allow the temperature to fall to 400°, then add 10 lb. of granulated manganese oxide, and when dissolved sprinkle in 10 lb. of litharge and 10 lb. of red lead. Boil for ½ hour at 475°, then add 6 lb. powdered burnt umber and 5 lb. of gum shellac. Boil to 500°, then cool and reduce with 80 gallons of turpentine.

2. ROSIN GRINDING JAPAN.

500 lb. K rosin.
25 ,, powdered air-slaked lime.
2 oz. beeswax.
70 gallons benzine.

Melt the rosin, sprinkle in the lime gradually until it is taken up by the rosin and the sediment settles. Add the beeswax and allow the mixture to simmer ½ hour over a light fire. When sufficiently cool add the benzine, being careful that it goes into solution without granulation.

3. GLOSS OIL.

500 lb. K rosin.
7½ ,, lump umber.
2½ ,, black oxide of manganese.
1¾ ,, brown sugar of lead.
10 gallons kerosine.
60 ,, benzine.

Melt the rosin. Mix the manganese and sugar of lead and boil 1 hour in the rosin, stirring occasionally. Crush the umber in a bag and suspend in the kettle, "dousing" it up and down from time to time. Boil until the manganese is incorporated. Take the kettle off the fire and add the thinners when the temperature has fallen to 250° or 300° according to the degree at which experiment shows them to take best. The kerosene is to be added first. In this, as in all the other formulas, complete absence of fire is, of course, a requisite to the addition of the "thinners".

DRIERS.

4. PURE TURPENTINE JAPAN.

16 gallons well-settled and aged raw oil.
25 lb. litharge.
27 ,, black oxide of manganese.
45 ,, kauri dust.
80 gallons turpentine.

Calcutta oil is generally preferred. Heat the oil to 350° F., then gradually sprinkle in the litharge, taking great care that it is thoroughly taken up in oxidising the oil. If the foam becomes thick it must be whipped down to prevent boiling over. Test samples on glass, and when the oil becomes syrupy to the touch, add the manganese oxide, for which an equivalent quantity of the borate may be substituted if a light colour drier is required. The manganese in combining generates heat, and if necessary the fire can be drawn and the kettle taken off when the temperature of 550° is reached. The manganese must be sprinkled in very gradually, as it will cause the oil to swell up very rapidly. When all the ingredients are in test samples on glass. If right they should harden promptly and crack and break, but not powder when the film is bent double or rolled together. If they fly into powder the boiling is burned. The samples must also be elastic. When found to be right the kauri dust is to be sprinkled in, and samples taken out from time to time to see that no small particles remain undissolved. If necessary to effect this the kettle may again be run over a light fire. Samples of the finished product should crack as above explained. Extinguish all fire, and when the kettle has cooled to about 350°, reduce with the turpentine, one man stirring while another runs in the thinner as rapidly as it can be mixed. This makes a very strong drier if properly prepared.

5. BENZINE JAPAN.

12 gallons linseed oil.
16 lb. litharge.
16 ,, powdered black oxide of manganese.
10 gallons turpentine.
75 ,, benzine.

The entire 85 gallons of thinners may be benzine, but a small proportion of turpentine makes the reduction easier. The process of preparation is similar to those already detailed.

6. UNION JAPAN

May be made on this formula by using for thinners about ⅔ turpentine and ⅓ benzene, or ½ of each.

7. WHITE DAMAR VEHICLE FOR ENAMEL PAINTS.

130 lb. Batavian damar.
15 ,, white rosin (W. W. or W. G.).
4 ,, sulphate of zinc.
12 gallons turpentine.
10 ,, benzine.

Melt the gum and the rosin with the zinc in a copper kettle until solution is complete. Add the turpentine gradually, while the kettle is on the fire. Boil for a short time; then draw the fire and reduce with the benzine. This product may be used as a varnish grinding with enamel colours, or as a white varnish pure and simple. It dries much harder than ordinary damar varnishes.

COBALT DRIERS.

It is claimed that fused and precipitated cobalt rosinates are similar in action to manganese rosinate with this very great exception, that by its use a better and finer white for inside and outside purposes can be secured.

For exterior driers it is claimed that, without the use of manganese and cobalt, there is a tendency to soften, due to atmospheric actions. Hence, the lead and cobalt or the lead and manganese compound is better; lead and cobalt in all cases where white quality is considered. For interior work cobalt is recommended as a drier, and it is urged that cobalt only be used.

Cobalt Rosinate Drier for Producing Good Exterior or Interior White Paint or Enamels.—Such a paint or an enamel made with either lead or manganese as a drier even if in only small quantities has a great tendency to produce a brownish or pink discoloration. Even so small a quantity as 16 oz. of manganese drier in 200 gallons of paint will show a pink colour inside of 48 hours. For exterior work this is not injurious, for strong sunlight bleaches out the colour; but for interior work we come to the fact that cobalt must be used to eliminate the discolouring effect. In making high grade enamels every one is familiar with the properties required. These can be secured by a cobalt drier made from wood oil, linseed oil, precipitated cobalt rosinate, and pure turps. It should be made in a separate pot, and strict attention paid to the handling of it. Such a drier is added to the enamel after the zinc has been ground into the varnish. But no other drier should be present. Working thus all trouble of skinning in the tin or in the mill is avoided, and no separation occurs with this oil drier.

If cobalt driers are very strong, they can be readily adjusted and kept for any length of time without separation. For cheaper whites, fused cobalt rosinate made on the same formula can be used; but there is the risk of paint livering or thickening, due to the free rosin acid present. A drier made thus can be thinned with a turpentine substitute. Litharge can also be incorporated in the fused rosinate, if a high grade colour is not particularly desired. The linoleate of cobalt can be used and will give quick-drying qualities like all cobalt compounds, but it does not give so nice a white and shows a tendency to skin. The white and light tinting enamels do not develop a pink colour when cobalt drier is used. But this drier must be prepared in a separate pot from the varnish. This kind of drier has the advantage over other driers, in that it gives an elastic, non-separating film when mixed with linseed oil, and is not injurious when used to excess. Cobalt drier will dry of itself on glass to the touch in 30 minutes, and become hard in 2½ hours. The quantity of drier to use varies with the varnish, but in general 1 part drier to 10 parts of varnish is used in straight long oil varnishes. With gum varnish 1 part to 20 or 30, and so used, will not increase the cost much. The increase is about 1 cent a gallon over that of a manganese turpentine drier. With the long oil varnish, turpentine drier should be used; but in enamels where damar varnish is present, one can use benzine or a cheaper turpentine substitute. Cobalt drier finds some use in interior paints, the pigment being ground without any other drier. The same formula thinned with a mineral spirit is an excellent drier for cheap whites.

In testing driers the ordinary organoleptic tests, lustre, smell, and hardness, etc., tell whether the drier is a rosinate or a linoleate. Mixtures of powdered driers may generally be separated by aid of the microscope, where the transparent rosin particles are at once seen. Moreover, fused driers are water-free, but precipitated driers contain a certain amount of water, as much as 6 per cent., which in the technical process of drying is not removed. Solubility in solvents is increased by expelling the combined water by fusing the rosinate. In qualitative testing for metals the drier is ignited, and the ash dissolved in HCl, and the filtered solution examined by the classical methods of qualitative analysis. To test for lime in possible presence of lead is utter folly, and *vice versa*. In addition to lead and manganese, calcium, barium, zinc, and copper may be present. Barium and calcium rosinates increase the hardness of the coating. Zinc rosinate is also used—it is claimed that it prevents the darkening of the boiled oil during heating. But a more intractable substance than precipitated zinc rosinate cannot well be handled. Copper rosinate is not used as a drier for boiled oil. Its use is in the hydrated state in anti-fouling compositions. A certain percentage of calcium rosinate, hardened rosin, its users claim, does no harm; hence linoleate of manganese is adulterated therewith, which is revealed by a qualitative examination of the acids. A certain portion of the drier is boiled with HCl, and when cold shaken with petroleum ether. The residue on evaporation is tested for rosin by the Storch-Morawski test. Finally, the physical and chemical "constants" are determined, and the abietic acid estimated quantitatively by Twitchell's method. Oleic and palmitic acid are only seldom used in the preparation of soluble driers. Still the presence or absence of such metallic compounds should be examined for.

In estimating the metals soil or dirt should be absent. Sand often occurs as an impurity.

[German writers tell us, quoting Coste and Andrews, "Analyst," 1910, 35, 54, as authorities, that "soluble driers are often mixed with chalk and barytes". But there is a little misapprehension here. The driers referred to by Coste and Andrews were the old-fashioned "patent" driers marketed in the same manner as stiff white lead (that patent must be a very hoary-headed one, and as far as the actual manufacture is concerned does not exist). These driers were made up as a stiff paint containing an excess of driers made in a rule-of-thumb way by heating linseed oil, rosin, litharge, lead acetate, etc., together; sometimes a saturated solution of manganese sulphate was added. The chalk and the barytes formed 90 per cent. of the mixture. "Patent" driers might therefore be defined as a paint with an excess of driers which, added in small proportion to a paint with no driers, caused it to dry rapidly.]

The main quality desired in a soluble drier is that it shall be completely and entirely soluble, the metal being in a state of actual combination, and not merely mechanically suspended in the form of an oxide, since the latter cannot exert any action at the low temperature employed, and will therefore merely constitute an inert, sedimental matter. The sole point, therefore, to be considered in estimating the value is the amount of drying metals present in combination with rosin or fatty acids, and soluble in linseed oil at 120° C.

Analysis and Valuation of Soluble Driers.—Soluble driers only containing lead are rarely marketed, nor is linoleate of manganese generally sold. The usual type of soluble driers on the market are :—

TABLE SHOWING THE USUAL TYPE OF SOLUBLE DRIERS ON THE MARKET WITH THEIR PERCENTAGE Pb AND Mn CONTENT.

	Theoretical Metal Content per Cent.	Actual Range of Soluble Metal Content per Cent.
Manganous rosinate precipitated .	7·7 Mn	6·7 Mn
,, ,, fused . .	5·3 ,,	2·5 to 4·5 Mn
Lead manganese rosinate . .	—	8·9 Pb; 1·5 to 2 Mn
Manganese linoleate . . .	8·9	9 to 9·5
Lead manganese linoleate . .	—	Varies greatly

Meister quotes: (1) Fused Mn rosinate, on an average 2·5 to 3·0 Mn, = 45 to 55 Mn abietate. (2) Fused Pb Mn rosinate, at most 1·5 Mn, and 9 to 10 per cent. Pb, about 27 per cent. Mn abietate, and 40 per cent. Pb abietate. (3) Precipitated Mn rosinate, 5·7 to 6·5 per cent. Mn, about 80 per cent. Mn abietate. (4) Precipitated Pb rosinate, 20 to 23 Pb, about 80 per cent. Pb abietate. Some rosin driers barely contain 10 per cent. of rosinate.

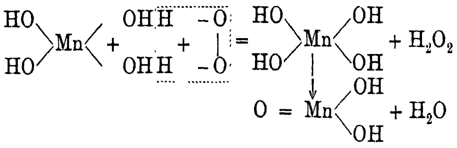
Practical Testing of Soluble Driers.—Analytical testing must be subordinate to practical testing of soluble driers, *vide infra.* The oil is heated with a certain amount of soluble drier to 120° to 150° C., and the resultant boiled oil tested for colour, clearness, rapidity of drying; or the drier is dissolved in a little warm turps, and 5 to 10 per cent. of the fluid drier so obtained added to cold linseed oil. The liquid driers used by painters and varnish-makers are in solution. Turps, rosin-spirit, benzine, benzol, are tested for in the volatile portion and the dried siccative. Generally liquid driers consist of solution of lead manganese linoleates 4 : 5, but manganese lead linoleate and rosinate are also used. The latter when added to boiled oil must contain no free rosin or it will thicken white lead paint. This is tested thus: 18 grammes pure white lead are rubbed up with 5 grammes of liquid drier, 2 grammes turps, and a drop of water. There should be no gelatinous thickening on standing for several hours.

Chevreul and Liebig versus Mulder.—Mulder studied how driers act very carefully, the result being some classical recipes for fire-boiled oil. But some plead that Chevreul did not understand the problem, as he used white lead and zinc oxide for driers, and later maintained that linseed oil dried more rapidly by mere heating to 79° C. Liebig believed that, at the outset, the drying of linseed oil was hindered by mucilage. He asserted later that linseed oil, treated with basic acetate of lead at the ordinary temperature, absorbs 4 to 5 per cent. of lead and dries in 24 hours. The best boiled oil was obtained by heating linseed oil to 100° C. with lead oxide, and steam passed through for an hour. By boiling linseed oil with lead oxide and water a similar good boiled oil is not obtained. All these assertions Mulder contradicted in a very bitter quarrel with Liebig.

Mulder's Theory of Oil-boiling and of Driers.—Mulder found that boiled linseed oil (with 2·6 per cent. PbO) took a shorter time to dry, but had a lower oxygen absorption than the unchanged oil. When the figures, as here, refer to very thick films, no sound information is obtained; but it is correct that linseed oil in the presence of a drier absorbs no more oxygen than without one; also that the drier, during the drying of the oil undergoes no change, it only hastens it. That red lead, as a drier, is superior to litharge he explained thus: Red lead is a mixture of oxide and peroxide, $2PbO$, PbO_2, and therefore contains available oxygen, which it gives up to the oil with formation of linoxic acid or lead linoxate, then the oil absorbs no more oxygen from the air. Litharge, on the other hand, cannot part with any oxygen, and the oil must get it from the air unless the oil be boiled with litharge, whilst a current of air is passed through it. Mulder does not speak of oxygen absorption in connection with litharge, but he does so in regard to manganous borate. He found that when a borax solution was precipitated by manganous sulphate, and the precipitate washed with water, the surface is coloured brown owing to the absorption of oxygen. It follows therefore that manganese borate as a drier acts similarly, taking oxygen from the air and giving it up to the oil. The term catalyst was unknown to Mulder, as it was not used until later. He was, of course, acquainted with catalysis in the sense used by Berzelium and with Mitscherlich's contact working. Later on Ostwald classified sharply and positively as catalysts only those substances which during a chemical reaction hasten it by their presence. Their working has been likened to that of a lubricating oil during the motion of a steam engine. Weger also investigated the drying action of manganous borate, and discriminated betweer it and all other insoluble driers, by its being capable of being used a the ordinary temperature when it is intimately mixed with linseec oil. By rubbing up linseed oil for an hour in a mortar with 5 pe cent. of manganese borate, the time of drying was 6 to 24 hours the filtered oil contained 0·05 to 0·10 per cent. Mn. To classif manganese borate in face of this Mn content as an insolubl drier is a gross misuse of terms. Whether the salt dissolves i completely acid-free linseed oil, Weger leaves undecided. In an case, manganous sulphate, which is but slightly decomposed on heating when rubbed with linseed oil, only acts slightly and similarl when precipitated as $Mn(OH)_2$. That driers, as such, are all catalyst Weger deduced from the fact that the drying capacity of linseed oil i not proportional to the amount of drier used, but with a certain weigh of drier a maximum result is obtained. Again Weger contradicts a statement of Chevreul that a mixture of raw oil and manganese boiled oil absorbed more oxygen than its components, assertin that the final result would be that an oil would absorb so much mor oxygen the less manganese it contained, and his oxygen absorptio experiments did not confirm this. It is strange if the oxides and salt of lead and manganese act very similarly as driers, how dissimilar bot these metals are.

Van Zoul experimented with manganese peroxide. He foun that it could not work catalytically as it is reduced on heating wit linseed oil. He thinks that during the splitting up of linseed oil th oxygen of the linoleic acid becomes oxidised as in the Hazura oxidation, and that the resulting hydrolysed acid, in the form of a manganes salt, acts as an oxygen carrier. He therefore regards all the acid produced during the oxidation of linoleic acid in alkaline solutio as good driers. He does not say why manganous oxide is a goo drier.

Engler and Weisberg's Autocatalysis.—Engler and Weisber describe the catalytic phenomena which occur during autoxidatio decomposition as autocatalysis, and the oxygen carrier as an autocatalyst. They thus distinguish between atomic or hemi-molecular an molecular autocatalysis. At the first comes the catalyst, in our cas the drier, which takes oxygen from the air in molecular form, an acceptor, and later on gives it up in this case to linseed oil. Molecula autoxycatalysis is identical with indirect autoxidation, where th molecular oxygen reacting body (indirect autoxidiser) first, throug this reaction, forms a third body. The drier, in that case, acts as pseudo-catalyst. Thus there are bodies which, through the agency other bodies by the consumption of negative ions or by the disengag ment of positive ions, start the right atom-forming reaction which, o its part, carries on the autoxidation. Such atoms are mostly hydroge atoms which as indirect autoxidisers absorb molecular oxygen a produce hydrogen peroxide. As an example take the catalyt working of manganous hydrate in the Weldon regenerating process, which Engler and Weisberg formulate thus:—



Catalytic action of Weldon process (Engler and Weisberg).

Here water intervenes, whilst in drying it does not, except in a secondary way as a bye-product.

According to Hazura from linseed oil two different hydroxystearic acids are obtained, the first from linolenic acid, the other an unsaturated fatty acid with three double links, isolinolenic acid, $C_{18}H_{30}O_2$, an isomer of linolenic acid. With bromine it yields, according to Hazura, an oily hexabromide derivative soluble in ether. Were it not for isolinusic acid the occurrence of isolinolenic acid in linseed oil would have been still unknown; likewise that the unsaturated fatty acid can yield two different oxyacids.

It will be seen therefore that the result of Hazura's researches was to put the chemistry of linseed oil on a new basis. Whilst all previous authors, with the exception of Mulder, regarded the fluid linoleic acid as a single substance, Hazura found it to be a mixture of four acids, viz.:—

1. Oleic acid, $C_{18}H_{34}O_2$, with 1 double link.
2. Linoleic acid, $C_{18}H_{32}O_2$, with 2 double links.
3. Linolenic acid, $C_{18}H_{30}O_2$, with 3 double links.
4. Isolinolenic acid, $C_{18}H_{30}O_2$, with 4 double links.

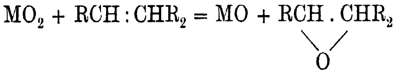
Reformatsky and the Unity of Linoleic Acid.—None the less the unity of linoleic acid was still maintained. From Saytiff's laboratory there appeared a research on linoleic acid by A. Reformatsky. He prepared it by Schuler's method, converted it into the ethyl ester, and fractionally distilled the latter under a pressure of 180 mm. The fraction 270° to 275° C. was collected apart and saponified. For the free acid the composition of linoleic acid was found to be $C_{18}H_{32}O_2$; it gave an oily tetrabromide. On oxidation in alkaline solution with permanganate it yielded as chief product a tetraoxystearic acid of melting-point 159° to 161°. When H_2O_2 is formed as an intermediate product, it can only yield atomic oxygen to the oil. Both lead and manganese driers produce peroxides. Whether drying is a hemi-molecular or a molecular autocatalysis is undecided. From the high oxygen absorption of boiled oil, at any rate, atomic oxygen is not exclusively absorbed. Ostwald confirmed Genthe's conclusion that in drying with or without driers autocatalysis occurs. The catalyst supervenes when linseed oil is heated in air, when it is converted into a quick-drying boiled oil. Drying is hastened by light. When ground up with white pigments oil dries more quickly than with black ones. Looking to the S form of the curve, the results compared with Ostwald's formula for autocatalysts $\frac{dx}{dt} = K(m + x)(a - x)$. A series of researches were made on exclusive autocatalysts. To linseed oil 1 per cent. of formic, acetic, propionic, valeric, crotonic, cinnamic and oleic acids were respectively added; energetic oxygen absorption occurred during 8 to 10 days, and the curve was still S shaped. Similar results were given by glycerine, benzaldehyde, mesityl oxide and acrolein. Whether the catalyst is affected by the volatile reaction products was to a large extent solved thus: a uviol glass tube was filled with pieces of sulphur, soaked in linseed oil in an air-exhausted space. Parallel with this tube, about 3 centimetres away, was a uviol lamp. Over the pieces of sulphur a rapid current of dry oxygen was passed, and the evolved gases cooled in a Dewar's apparatus to 20° C. In about 48 hours about 1 gramme of a strongly acid fluid had condensed. But oil treated with 1 per cent. of this fluid did not dry any quicker, as occurred when 50 grammes of linseed was exposed in a large clock glass to uviol light for 40 hours. An oil exposed for 1½ years in a loosely-corked flask, also an oil blown for 2 hours at 130° C., both dried faster, so that when boiled linseed oil is oxidised the autocatalyst is a peroxide. Thus 1 per cent. of benzoyl peroxide greatly hastened drying whilst ethyl peroxide hastened it but little, and hydrogen peroxide not at all. Five per cent. of fresh turps in no way increased the rapidity of drying, but, on the other hand, 5 per cent. of old turps did so very greatly. As the particles first impinge on linseed oil, and oxygen has already been absorbed so as to darken the oil, the curve approaches a straight line. The principle does not allow an unlimited concentration of catalysts. For the acceptance of the oxygen a peroxide is necessary. Circumstances all point to the practical limits of the reaction sought, being independent of the oxygen concentration. Thus in the dark the same result is obtained in air and oxygen, showing the enormous effect of light.

Examination of Driers.—Genthe tested lead and manganese oleate, then fused and precipitated manganese rosinate, fused lead linoleate, fused manganese linoleate, fused lead manganese rosinate, fused and precipitated lead manganese linoleate, fused copper rosinate. They were dissolved in the proportion of 1 per cent. in warm linseed oil. Sometimes they separated out as a jelly-like precipitate, which on shaking separated into finer particles which seemed to have fallen out of the oil, possibly mucilage. The drying process lasted from 14 to 50 days in the dark, in day-light 8 to 10 days. The acceleration of drying is therefore not so great as is generally believed; however, the S form of the curve persisted throughout. The autocatalysts remain whatever the driers may be; they are not to be confused with the pseudo-catalysts. In violet light the driers were completely without action. On the basis of the last discovery, Genthe issued a statement from which it appears established that during drying peculiar peroxides are formed, either when the oil solidifies under the action of the oxygen of the air, or when the oil at the anode pole becomes proportionately oxidised, as the peroxide building proceeds, e.g. in weak alkaline glauber salt solution with lead electrodes. The formation of peroxide compounds is the essential point of the drying properties of accelerating catalysts; hence all other driers are only pseudo-catalysts, the function of which is the formation of the former accelerators. The linseed oil products are valuable as the quickly formed coating is uniform throughout the whole thickness of the film, right through without skinning and cracking, forming a lustrous enamel-like coat. The dried layer is not tacky but hard and resinified.

S. A. Fokin states that catalysts reduce the time of drying from 4 or 5 days to 2 to 3 hours. He tested the behaviour of 15 metals in this respect with the following results:—

1. Co, Mn, Cr, Ni, (Fe, Pt, Pd).
2. Pb, Ca, Ba.
3. Bi, Hg, Ur, Cu, Zn.

This assortment, in which lead comes after iron is in flat contradiction with the results obtained in actual practice. Fokin explains the action of driers in this way; that the metals in their higher oxidation compounds take up atomic oxygen and give it up to the oil according to the formula:—



$$\mathrm{MO_2 + RCH{:}CHR_2 = MO} + \underset{\diagdown\,\mathrm{O}\,\diagup}{\mathrm{RCH\,.\,CHR_2}}$$

When direct autoxidation with absorption of molecular oxygen is practicable, only a small amount of drier, or a weak drier, is added. The rapidity of reaction is proportional to cube root of concentration of catalysts. Oxygen absorption at from $\frac{1}{5}$ to 20 atmospheres is proportional to pressure. Increase of temperature hastens rapidity of reaction, according to Spring's rule. Polymerisation proceeds along with oxidation. In later experiments Fokin contradicts Genthe. He first made an experiment in which cobaltiferous linseed oil (0·36 per cent. Co) was put into a Hempel burette and treated with gaseous oxygen. The results obtained for absorption of 1 atom of oxygen per double bond cannot be regarded as free from objection. At one time the oxygen was used in slight excess; again, the layer of oil was not presented to the oxygen in a thin enough layer, and no notice was taken that the iodine number was never 0. Moreover, in the above research the statement that 1 per cent. of the linseed oil forms volatile substances can hardly be regarded as correct. Fokin later on tested a large series of boiled linseed oils on glass slabs, on which the film rose to 5 mg. per sq. cm. He asserts that the same absorption figures were obtained, whether he used 0·5 or 5 mg. But the test in question only lasted 2 hours and with the intervention of a weight of fungi of $\frac{1}{100}$th part of a milligramme and in two cases of $\frac{1}{1000}$th part of a milligramme. The unreliable nature of the experiments will be seen in a moment from the excessive thickness of the layer, and we agree with Weger that the thickness should not exceed 1 mg. per sq. cm. Fokin obtained for cobalt-boiled oil of varying Co content in 2 to 10 hours oxygen absorption of 9·1 to 15·4, whilst the oxygen absorption figure for manganese-boiled oil in 41 hours was 18·1. The results obtained did not establish Ostwald's autocatalytic equation but rather one of Fokin's defunct formulæ. That the reaction is not proportional to the catalytic concentration is explained by diffusion. Some of Genthe's results show that the relation $\frac{dr}{dt} = K(a - x)$ corresponds best for monomolecular reactions. It must be pointed out that Genthe was incorrect when he used the term indirect autoxidation and that the formation of autocatalysts is dubious. Drying is rather a hemi-molecular autocatalysis, the drier absorbing by means of its valency surrounding oxygen and then giving it up in atomic form to the oil. Fokin's results are faulty also in his tests on glass slabs, considerable quantities of volatile substances escaping.

CHAPTER XIV.

BOILED OIL.

Linolein.—As all oils consist of carbon, hydrogen, and oxygen in almost identical proportion, what principle is absent from non-drying oils is present in certain oils, which causes them to dry. Linolein, according to Mulder, is the chief constituent of such typical drying oils as linseed, poppy-seed, and walnut oils. Linolein consists, therefore, of linoleic acid and glycerine, the compound formed by the union of three molecules of the monobasic acid, linoleic acid uniting with one molecule of the triacid base, glycerine, to form the neutral salt linolein. Hazura and Fredreich, who found in poppy-seed and walnut oils fatty acids similar to if not identical with linoleic acid, partially confirmed Mulder's conclusions. Hazura regards Mulder's linoleic acid not as a simple substance but as built up of two distinct acids, linoleic acid, $C_{18}H_{32}O_2$, with two double links, and linolenic acid, $C_{18}H_{30}O_2$, with three double links. The triglyceride trilinolin is represented by the empirical formula, $C_3H_5(C_{18}H_{32}O_2)_3$, and the triglyceride trilinolenin, $C_3H_5(C_{18}H_{30}O_2)_3$. Livache flatly denies that the drying properties of linseed oil are entirely due to the presence of any one or all of these acids. All other oils, he contends, whether vegetable or animal, can be transformed into a solid product, analogous to that to which linseed oil is so easily converted, and that, whether taken individually, or as the component parts of a mixture, provided always they be subjected to the action of heat. Livache is not specific enough as to what he means by the action of heat, and his claims do not amount to much, as it has long been known that certain non-drying oils can be stored so as to yield a protective film. Moreover, a rosin varnish made by dissolving rosin in naphtha and then applying the varnish so obtained, whilst the bath or water oven is boiling over its outer copper surface, will protect the latter from the fumes of the laboratory remarkably well, but that does not endow rosin with the properties of a drying oil. Again, Angus Smith simply recommended coating water pipes with tar and baking before laying them, but that did not make tar a drying oil. Livache's idea must fall flat as his coating can in no way have the insolubility, impermeability, nor durability of linseed oil.

None the less Livache declares that the best explanation that can be given of the drying properties is the following: All the different glycerides which enter into the composition of a drying oil play a part in the transformation of the oil into a solid body, but the greater the proportion of one or several glycerides analogous to linolein, the more rapidly is this transformation effected and at a lower temperature. All the glycerides present in oils and fats undergo this change more or less slowly, as if by a kind of metamorphosis. This doctrine cannot be upheld for very obvious reasons, upon which it would be futile to enlarge.

Looking at the matter from his own standpoint, Livache tried to explain the differences—in drying properties—of different drying oils. Should in fact the glycerides, analogous to linolein, be present but in small quantity, the other glycerides only dry slowly, and very often heat would be required to accomplish the end in view. Whatever explanation we adopt, we must bear in mind that the drying oils are those which may be quickly converted into a solid elastic substance at the ordinary temperature. This transformation only takes place in the presence of oxygen, and with a rapidity which varies according to the heat and light to which the film of oil is exposed, and the previous treatment to which it has been subjected.

Linoxin.—Mulder called the resulting solid product *linoxin.* He found that it did not differ from linoleic acid except by containing a larger proportion of oxygen, whilst at the same time all the glycerine had disappeared. While making reservations necessitated by the still imperfect state of knowledge regarding the composition of the different solid bodies obtained by the oxidation of different oils, the name of linoxin is here retained for this body, which, no matter from what oil it may be derived, presents the same properties of elasticity, insolubility in the usual solvents, etc. Linoxin consists of a perfectly dry elastic mass, of a more or less deep yellow or brown colour according to the treatment to which the oil from which it has been derived has been subjected. For a long time it was believed to be perfectly insoluble in the different menstrua in which oils dissolve. When exposed to their action it at first undergoes no change, but if the action be prolonged it increases in transparency, swells like india-rubber, and at the same time a small proportion dissolves. The resulting swollen substance dried apart from the solvent is still elastic, but very friable between the fingers, crumbling to particles, with no tendency to reunite. By evaporating the solvent there is left a tacky residue of low melting-point. The oxidation product of a drying oil, therefore, presents many analogies to caoutchouc, being composed like it of two constituents, one of which dissolves in different menstrua, whilst the other swells and disintegrates. The dissolved product recovered on evaporation of the liquid solvents acts as a real cement, reuniting the insoluble portions, first swollen and then disintegrated, yielding as a result a continuous elastic mass, consisting on the one hand of the soluble, and on the other hand of the insoluble, portion of the original linoxin. But very possibly this liquid portion found by Livache was simply incompletely oxidised oil, or the residuum of the saturated fatty acids naturally present in linseed oil, which the writer contends do not dry in themselves, but retard the drying of the oil until the intensity of the reaction is such that the solidified glycerides give to the whole mass the appearance of one homogeneous solidified coating, the actual non-homogeneity of which nothing discloses until the solvent starts to act on it. Thus before an oil can dry, continues Livache, the linolein must be in a position to become oxidised, and the more this is facilitated the quicker does the oil dry.

Oxygen may be caused to act either upon the linolein, i.e. upon linoleic acid combined with glycerine, or upon the linoleic acid separated from glycerine, or finally upon suitable chemical combinations of linoleic acid with metallic oxides, i.e. upon linoleates.

Action of Oxygen upon Linolein.—Linseed oil exposed to the air in a thin layer soon changes to a solid substance. If we perform the same experiment in a vessel containing air placed mouth downwards over mercury, the same change takes place, but the volume of air confined over the mercury diminishes in volume owing to the absorption of oxygen. Finally, if the quantity of air suffices, the oil is converted into a solid product which has increased in weight proportionally with the oxygen which existed in the air and which has disappeared, whilst the residual gas is composed of nitrogen, together with a small quantity of carbonic acid, and volatile acids of the methane series. The transformation of the oil and consequently of the linolein is thus due to the action of oxygen. Mulder obtained this solid body by exposing the oil on plates to the action of the air, and after detaching, he treated the product with ether, alcohol, and water so as to wash away any unoxidised oil or other soluble matter; and he finally obtained a more or less elastic white substance which analysis showed to be a product of the oxidation of the anhydride of linoleic acid, viz. linoxin. From linoleic acid exposed in a thin layer to the air he obtained the same solid linoxin, but the change into a perfectly dry substance took longer than in the case of linolein. But the products are identical in composition and properties, and as no glycerine is found in the product of the oxidation of linolein by the air, it would appear that the oxygen of the air first acts upon the glycerine, yielding such bodies as carbonic acid, water, etc., which disappear, and subsequently upon the linoleic acid of the linolein, converting it into a solid body, linoxin. The product is identical whether we use air or oxygen.

Action of Oxygen upon Linoleates.—Linolein is very easily saponified, yielding soaps; potash, soda, and ammonia yield soaps which readily dissolve in water. Baryta, lime, the oxides of zinc, copper and lead, yield soaps insoluble in water but soluble in ether. The most suitable combination to study is that of linoleic acid with oxide of lead; if we dissolve this linoleate of lead in ether, and if we expose the liquid in a thin layer upon a plate of glass, the white solid residue remaining on evaporation of the ether, which is at first soft, becomes in a few days very hard, owing to the absorption of oxygen.

Linoxic Acid.—If we suspend this hard, brittle salt of lead in alcohol, and pass a current of sulphuretted hydrogen through the alcohol, we obtain, after filtering off the sulphide of lead, an alcoholic solution from which water precipitates a white substance, which analysis shows to be that oxidation product of linoleic acid to which the name of linoxic acid has been given. If instead of separating this alcohol in the cold by the simple addition of water, we evaporate the alcoholic solution by the aid of heat, we also obtain a viscous residue, but of a blood-red tint. Linoxic acid is therefore met with in two colours—white or red—according as it has been prepared in the cold or the hot state, i.e. whether hydrated or anhydrous. But whilst viscous linoxic acid exposed to the air changes to dry elastic linoxin, on the contrary, when combined with lead—although it also suffers this alteration—it becomes more and more friable.

Résumé.—(1) *Linoleic acid* combined with glycerine, in the state of *linolein*, yields progressively in a more or less short period of time *linoxin*, a solid elastic body, a basis for colours and varnishes. (2) Free linoleic acid yields fairly quickly a viscous compound (linoxic acid) which afterwards changes to linoxin, but occupying a longer period of time than in the preceding case. (3) Linoleic acid combined with oxide of lead, i.e. *linoleate* of lead, dries fairly rapidly in consequence of the formation of *linoxate* of lead, but this product changes afterwards into a friable, brittle substance. It follows that, to ensure a dry, elastic product, we ought preferably to cause the oxygen to act upon the linolein and to avoid, as far as possible, either the presence of linoleic acid, which would take a longer time to dry, remaining viscous for rather a long time in consequence of the formation of linoxic acid, besides the possibility of formation of linoleate of lead, which would give a brittle, friable product. Owing to the difficulty of separating linolein from the other principles entering into the composition of oils in actual practice, we have to oxidise the oil itself. The drying properties of a drying oil are increased under certain conditions, which it is important to study in detail. We shall study, therefore, how the drying properties of linseed oil—the best drying oil—may be increased, for whatever we may determine regarding it holds good, keeping to the same proportions with other drying oils.

Boiled Linseed Oil.—Linseed oil is boiled in several different ways: 1. *Fire-heated Boiled Oil.*—By boiling linseed oil at 250° to 465° F., in cast-iron pots fixed in masonry, or in portable pots over an open fire. 2. By boiling the oil at 270° to 300° F., not by direct fire but indirectly, that is to say, by a steam heat in steam-jacketed pans, some of which are open and others closed, by a dome fitted with a still heated connecting pipe, leading to a condenser. The oil is then agitated so as to break it up or effect division into fine drops, by agitators with blades like the propellor of a ship, so as to facilitate the action of the air on the oil. 3. By boiling the oil in closed vessels fitted with air pipes, and then blowing hot air through the liquid. 4. Boiling by steam superheated to 750° F.

Danger of Fire and Explosion.—Oil-boiling by heat from an open fire is particularly dangerous, but whichever of these processes be adopted, oil-boiling is always a more or less dangerous operation. Process 1 is the most dangerous of the four, as fires with open grates are difficult to regulate, and this difficulty of regulation extends to the product being heated. The first risk to draw attention to is one common to all the four processes: linseed oil, long before the actual boiling-point, not the apparent boiling-point is reached, liberates, between 300° and 600° F., not only vapours which ignite spontaneously, but also explosive vapours. Moreover, it is apt to froth and boil over, especially when it is impure, abounding in mucilage. The temperature increases very irregularly over an open fire, and the oil in the pot frequently bumps, especially as the heat intensifies, when dangerous priming may suddenly occur. Finally, the oil, or the added material driers, readily burn on to the sides of the pot, bake to a hard cake, causing the pan to grow red-hot, which readily gives rise to an explosion. Linseed oil becomes linoxin, dried linseed oil, when it

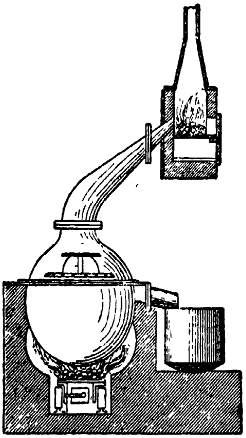


FIG. 82.—Oil-boiling by fire. Consuming the vapours by passing them through a fire.

has taken up and absorbed a certain amount of oxygen that become saturated therewith. Of this gas it is able to absorb and fix somewhere between 20 and 30 per cent. of its own weight (*vide supra*). This absorption occurs not only during boiling, but afterwards, and to a still further extent when the boiled oil is exposed to the air in a thin film. As to the fixation of the oxygen of the air by the raw oil, or by the oil boiled without driers, numerous attempts have been made to accelerate the drying of the raw oil, or even the oil boiled without driers, by adding to the oil substances rich in oxygen, such as pyrolusite, manganese borate, litharge, and red lead. With such accelerators of the drying of linseed oil as these are, the drying can be completed under 20 hours where it formerly took several days.

Driers of this nature (metallic oxide driers) require to be heated to a high temperature before they dissolve in the oil. The pert question as to the exact temperature at which litharge dissolves in linseed oil is easier asked than answered. The blowing of linseed oil also aids in the rapidity of drying, and thus assists the various oils in drying, and if the oil be blown in contact with a drier, it not only re-oxidises the drier, but aids very materially in its solution in the oil. So long as linseed oil is not completely oxidised, and such an oil is used for the coating of porous fibrous goods like textiles, feathers, papers, artificial flowers, millboard, etc., the process of oxidation continues until the oil is completely dry, during which time a very considerable amount of heat is generated. As long as this heat is not concentrated into a confined space but is dissipated into the air as fast as formed, the risk of accident is less to be feared. But if, on the other hand, the articles coated with this oil be kept stored during drying, or are so packed that the heat is prevented from escaping, the heat so retained and concentrated will eventually produce charring, and end in the spontaneous (ignition) combustion of the articles so coated, just as occurs in the case of greasy rags. Dusting the goods with wool dust, a bad practice, intensifies the risk.

Linseed oil can be caused to dry more rapidly by different processes, some involving the presence, others the absence of water. The action of heat as well as that of certain oxides or metallic salts, especially the salts of manganese, lead, and zinc, greatly lessens the duration of the operation. By simply exposing linseed oil in thin layers (2 to 3 cm. in thickness) to the action of the sun for several months in leaden vessels with a flat bottom, a thick and almost colourless oil is obtained. This is washed with boiling water to eliminate the acid principles, and after decanting and fresh exposure to the sun for 8 days in leaden vessels, a pale white, limpid, and more rapidly drying oil is finally obtained.

The presence of porous bodies seems to facilitate the production of rapid drying oils. Thus by treating linseed, walnut, or poppy-seed oil with snow so as to form a solid mass, and by putting this into earthenware or porcelain pots with wide mouths, and placing these in a cool place sheltered from the sun's rays, two layers are obtained on thawing, one of which is aqueous and the other oily. The oily layer is turbid, but easily clarifies on standing. It possesses more rapid drying properties corresponding with the length of contact with the snow. It must not be forgotten that snow brings down nitrous and nitric acids from the air, and that these reagents rapidly oxidise linseed oil.

Simple heating with ebullition of 3 hours and firing of the oil for 2 minutes produces more viscous drying oils in a quick way. The operation presents several dangers, in that the oil easily takes fire and that, moreover, the disengaged vapours are noxious. These should be burnt as completely as possible. The temperature during the boiling should not be too high, otherwise the oil will darken greatly and lose in quality and in value.

Certain writers recommend that linseed oil should be boiled in the presence of water, whereas others condemn this practice, pointing out the difficulty of clarifying oil so treated. Without doubt the presence of water lengthens the operation, but this expenditure of time is compensated for by the state of the oil, which is colourless and may even be obtained in a quite limpid condition, when at the end of the operation the greater part of the water is evaporated off by means of additional heat.

The majority of makers commence by heating the oil to a temperature bordering upon boiling (about 150° C.) before adding the driers. When this method is adopted a boiling pan large enough to allow for the augmentation of volume produced by the expansion and frothing of the oil must be provided, and the driers must be added by degrees and in as dry a state as possible. This is why certain recipes, without stating reasons, recommend the employment of calcined substances, whereas it is claimed that a product of quite as good a quality can be obtained by putting the ingredients into the oil before the fire is lighted. It is better, even in this case, to employ perfectly dry material.

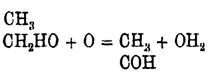
Some makers put the driers into a bag, whereas others, following the very early example of Watin, mix up the ingredients and the oil. The results are equally good in either case.

In discussing the question whether varnish-makers who cater for a mixed trade should supply their customers with boiled oil of their own make or purchase what they require for this purpose, Huenchen points out that makers in a large way of business have the requisite plant for boiling oil themselves, and that by doing so they can secure the margin of profit on the boiling, whilst at the same time they are certain of letting their customers have a genuine article. A good deal has been written on the necessity for supplying pale boiled oil; but in reality the demand for this grade is not extensive, and is only suggested by the continuance of offers. A point of greater importance than colour is that the oil shall dry well, and furnish a durable coating;

for the surfaces to which it is applied. In the manufacture of oil varnishes, boiled oil plays only a minor part, raw linseed or thick boiled oil being chiefly used nowadays; and in this connection it may be mentioned that linseed oil which becomes flocculent when boiled may be utilised for boiled oil, though quite unsuitable for varnish. While good boiled oil can be obtained with the aid of litharge, the use of this drier results in a good deal of foots; whereas, when half the quantity of hydrated oxide of manganese or manganese borate (1 to 1½ per cent.) is used, the deposit is much smaller. Similar results follow the employment of such driers as the rosinates of lead and manganese, and these latter have the additional advantage that the oil only needs heating to 120° to 180° C., as compared with 220° to 240° C. when the oxides are used. For the varnish-maker it is an advantage to prepare his own driers, since he has all the appliances at hand, and can in this way reduce the cost of his boiled oil.

The Function of Ozone in Causing Linseed Oil to Dry More Rapidly.—Drs. Schrader and Dumeke used ozone not only for bleaching amber and other varnishes, but to hasten the rapidity of drying of linseed oil or turpentine, and for the rapid bleaching of linseed oil. By passing ozone through oil contained in deep and narrow vessels, the action is finished in a relatively short time, and the oxidation ceases almost completely. If the oil is then exposed in shallow vessels to sun and air, further oxidation occurs, the bleaching and the thickening of the oil are hastened and the rapidity of drying is increased. In the manufacture of boiled oil the addition of a few hundreths of finished boiled oil to the linseed oil to be used facilitates the fixation of oxygen, and an action occurs similar to oil-boiling catalysis. In practice the linseed oil is mixed with a small proportion of previously made boiled oil, and a current of ozonised air is then driven through it by a pump, the oil being placed in tall and narrow vessels, which are heated by steam during the process. In a short time a white rapidly drying oil is obtained. In Pummerer's process the oil is rendered colourless and transparent, and its drying power is increased by subjecting it, with or without heat, to the action of a current of ozone in closed vessels. Pumps force or suck the gas through the oil until it ceases to be absorbed. The oil to be oxidised may be placed in receivers heated to 40° to 50° C. by a coil. The ozone enters at the bottom through a number of small holes so arranged as to make the contact between the ozone and the oil as intimate as possible. Certain piano makers use ozone for boiled oil. In his process for drying varnished marquetry, Carl Hoch places the articles in an oven, and ozone is made to pass over them through pipes. Whilst Japanning requires a temperature approaching 300° C. (572° F.), one of 35° suffices for the Hoch process, which can then be employed with objects that it is dangerous to make very hot.

Acrolein is a product of destructive distillation, and as oil-boiling is partially a destructive distillation product, acrolein is produced during oil boiling. It may be regarded as a toxic product. It is especially abundant in crude wood spirit. Prior to the Excise granting the use of methylated spirit for industrial purposes, the crude wood spirit used by French polishers so abounded in acrolein that many of them—and quite young men too—went blind. The remission of the ordinary fiscal tax on denatured alcohol was dictated by humane considerations wholly and solely. For many a long year in America, up to about a decade ago, acrolein counted among its annual victims hatters and French polishers, although they have long had in America a pure methyl alcohol free from any trace of acrolein, but acrolein still counts its victims amongst the engineers who attend to a leak in the fractionating stills in which crude methyl alcohol is rectified. A whiff of concentrated acrolein from a leak places them *hors de combat* for a week. Acrolein is not only produced during oil-boiling by steam but also in oil boiling by fire. It is quite a persistent product in both cases, the only consoling thing about it is, if it nearly kills the tyro in oil-boiling, it none the less does him a very good turn indeed. While his eyes are weeping copiously and smarting acutely and his nose discharging in streams, he can congratulate himself at being in at the death of that highly cunning old fox, the polymerisation theory. Even acrolein cannot be produced out of nothing. *Ex nihilo nihil fit*, and the tyro in oil-boiling has positive evidence of acrolein which belongs to the carbon compounds that are classed as aldehydes. And what is an aldehyde? Ah well, aldehydes are compounds intermediate between the alcohols and the acids. They are formed from alcohol by the abstraction of hydrogen; hence the name, which is an abbreviation of alcohol dehydrogenatum. *Preparation.*—The aldehydes are formed by the oxidation of the alcohols; ethylic alcohol, for instance, yields acetic aldehyde.

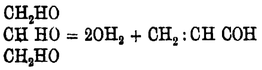


$$\begin{array}{ll} \mathrm{CH_3} & \\ \mathrm{CH_2HO} + \mathrm{O} = & \mathrm{CH_3} + \mathrm{OH_2} \\ & \mathrm{COH} \end{array}$$

Ethylic alcohol oxygen = acetic aldehyde + water.

Acrolein. Acrylic Aldehyde, $CH_2CH\ COH$, molecule weight 56.—One litre of acrolein vapour weighs 28 criths, boils at 52·4° C.

Preparation.—By the dry distillation of many organic substances as in oil-boiling and wood distilling. By the action of phosphoric anhydride or sulphuric acid, both of them dehydrating agents on glycerine.



$$\begin{array}{l} \mathrm{CH_2HO} \\ \mathrm{CH\ HO} = 2\mathrm{OH_2} + \mathrm{CH_2{:}CH\ COH} \\ \mathrm{CH_2HO} \end{array}$$

Reaction.—By oxidation acrolein yields acrylic acid—

$$\mathrm{CH_2CH\ COH} + \mathrm{O} = \mathrm{CH_2{:}CH(CO_2H)}.$$

Description of Actual Method of Preparation.—There are taken

	Grammes.
Anhydrous glycerine	200
Potassium bisulphate fused	500
Neutral potassium sulphate	200

The mixture is introduced into a litre flask with a short neck, the fused $KHSO_4$ being finely pulverised and the whole intimately mixed. The glycerine ought to be previously heated for some hours *in vacuo* at a temperature of 180° C. under a pressure of 50 mm. so as to be completely anhydrous. The neutral sulphate which is added afterwards is intended to fix the vapours of sulphurous anhydride which would completely polymerise the acrolein. The flask containing the mixture is connected with a good condenser, and the distillate is received in a large decanter surrounded by ice. The flask is heated on the sand-bath very gently during the first hour to avoid frothing and priming over into the condenser. The froth gradually disappears and the heat is increased so as to end the distillation in 3 to 4 hours. The acrolein separates on the top of the fluid distillate, the aqueous layer is removed as far as practical during the process so as to avoid too long contact with the acrolein. This aqueous solution of acrolein is heated on a salt-bath and the acrolein which distills is added to the upper layer, which is fractionated once or twice over precipitated lead oxide. To condense acrolein it is necessary to use iced water. The yield is 40 per cent. of the glycerine employed. Acrolein is a mobile liquid slightly soluble in water endowed with a piercing odour, which boils at 52·4 (126·32° F) under the atmospheric pressure. The only way to get quit of this highly toxic fume, so dangerous to the eyesight, is to pass all fumes and vapours containing acrolein through a furnace, or the oil-boiling pan should be on the top of the roof, or a hood superimposed over the pan leading the fumes to the condenser. The heat required to dissolve fused metallic rosinates in linseed oil is of too low a temperature to regard the production of acrolein in that particular process, yet in oil-boiling at a steam heat of 35 lb. pressure in a jacketed pan acrolein makes itself felt at an early stage, that is to say, under 248° F.

Dry Distillation of Castor Oil.—Under the action of heat castor oil yields ornanthol as well as a certain amount of undecylenic and polyundecylenic acids. The distillation is effected in a 2 litre green glass retort into which 500 grammes are poured and the neck of the retort is connected with a tubulated matras of 1 litre cooled by a current of cold water. This matras is connected by its tubulure with a vacuum pump and the aspiration so regulated as to maintain in the apparatus a pressure of about 100 mm. The retort is heated in an oil-bath until distillation starts and the temperature is so regulated as to keep it constant. First, ornanthol passes over along with water, then undecylenic acid bringing in its train a certain amount of its polymers. The heat is stopped when the froth formed reaches a height of about 5 mm. and the bubbles of gas can hardly make their way through the viscous mass. The residue being highly inflammable it is well to wait until the whole is cooled before opening the retort. The liquid distillate is fractionated on the water-bath under the same pressure of 100 mm. What passes over up to 100° C. is a crude enanthol. It is purified by fractionation at the normal pressure. The yield is about 10 per cent. of the oil employed. The residue remaining in the retort is distilled over a naked flame until the contents of the flask solidify. The temperature rises as far as 240 (464° F.), crude undecylenic acid is thus obtained, about 20 per cent. of the weight of the oil.

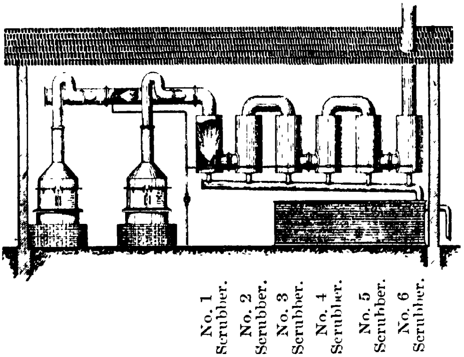

Pipe through roof through which harmless incondensable gases diffuse into air.

FIG. 83.—Two oil-boiling pots each set in its own brickwork furnace, each fitted with its own funnel-shaped dome. The latter is fitted to a pipe leading to another wider pipe through which a spray of cold water is injected under pressure.

Oil varnishes, boiled oil, and spirit varnishes, such as are prepared by means of a volatile solvent, dry in different ways. Linseed oil varnishes dry by absorption of oxygen from the air when an increase in weight occurs. Oil varnishes dry first of all by the oil of turpentine, used as diluent, evaporating, and the remaining mixture of resin and oil oxidising under the action of the oxygen of the air, and finally becoming solid and hard. Spirit varnishes with volatile solvents, such as oil of turpentine, alcohol, benzine, etc., dry by the solvent simply evaporating, and the resin, no matter of what kind, which had been dissolved therein, remaining behind as a firm coating. These facts are widely known, and form the basis of the manufacture of oil and spirit varnishes, but, according to experiments conducted by Andés, and described in the "Chemiker Zeitung," they only prove right if the boiled oil and oil varnishes are without admixtures of non-drying or very slow-drying substances and the spirit varnishes contain a single solvent of equal evaporative power in accurately set down limits. In the case of deviations from the above there will be other appearances. If, for example, boiled oil which by itself dries well, is mixed with a certain, but not very high percentage of mineral oil, an adulteration much in vogue, this addition will influence the drying capacity greatly, and it may occur that such a product does not dry at all. But if boiled oil is mixed with considerable quantities of mineral oil, a different observation will be made. The boiled oil applied in a thin layer takes up oxygen from the air and dries, and upon the dry varnish coating remains a thin layer of non-drying mineral oil. In the case of a mixture of equal parts of linseed oil, rosin oil rendered drying, and mineral oil, the same action was observable. Boiled oil and rosin oil became dry, while the mineral oil remained on the dried skin as a thin coating which might be wiped off. From this it follows that boiled oil takes up oxygen with separation of mineral oil and dries, a circumstance which deserves full attention in the examination of boiled oil, and which, without any analysis, demonstrates the presence of mineral oil in large quantities. If oil varnishes are prepared with solvents of different evaporative power, e.g. with oil of turpentine, which is adulterated with petroleum distillates, this does not exercise any other action but that to retard the hardening, i.e. the drying of the varnishes.

Oil-boiling by Direct Fire Heat.—Oil is still boiled to some extent and for special purposes in fire-heated cast-iron pans, often in the form of an inverted truncated cone, so that in priming the oil spreads over a wider area. Enamelled iron pans are also used, more especially on the Continent, but such pans are heavy and clumsy, and their use is not general in this country, where oil-boilers do not take to them kindly. The oil-boiling pan is half-filled with oil and heated for 3 hours. The oil is for certain purposes inflamed a few minutes before the fire is drawn. Again the oil is heated much higher, 200° to 225° C. (392° to 437° F.), and kept at that, sometimes it is said for 8 days, *vide infra.* So that the heat may not rise too high, a small quantity of tin is said to be sometimes added and care taken that the oil does not become so hot as to melt the tin, 228° C. (442·4° F.) but that would entail a constant watch on the oil pan unless obviated by an electric bell arrangement. For a thick oil the temperature is raised to 316° C. (say 600° F.) and kept thereat from 6 to 8 hours. But for pale boiled oil, it is not thought desirable to heat the oil so as to impart a brown colour to it and to liberate free linoleic acid, which dries more slowly than linolein. It has been urged that to produce a superior boiled oil the heat should not rise high enough to create destructive distillation of the oil on a wholesale scale, or to "crack" the oil, but should rather be kept at that temperature which brings about such change in the oil which would superinduce that very peculiar phenomenon known to purely theoretical chemists, and to them a height of about 5 mm. and the bubbles of gas can hardly make their way through the viscous mass. The residue being highly inflammable it is well to wait until the whole is cooled before opening the retort. The liquid distillate is fractionated on the water-bath under the same pressure of 100 mm. What passes over up to 100° C. is a crude enanthol. It is purified by fractionation at the normal pressure. The yield is about 10 per cent. of the oil employed. The residue remaining in the retort is distilled over a naked flame until the contents of the flask solidify. The temperature rises as far as 240 (464° F.), crude undecylenic acid is thus obtained, about 20 per cent. of the weight of the oil.

Pipe through roof through which harmless incondensable gases diffuse into air.

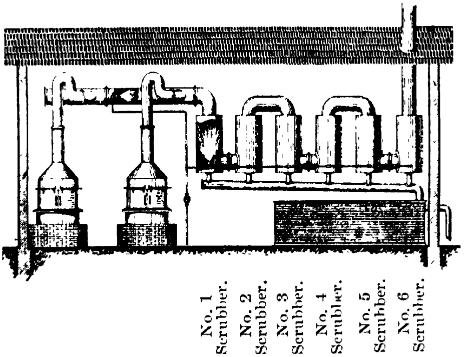


FIG. 83.—Two oil-boiling pots each set in its own brickwork furnace, each fitted with its own funnel-shaped dome. The latter is fitted to a pipe leading to another wider pipe through which a spray of cold water is injected under pressure.

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the pot fits. More often, the fire is underground, thus enabling the workman to watch the operation at his ease, since the pot is then on on the same level as the ground. In that case a rather different kind of pot (Fig. 84) is used, so constructed that the oil does not receive throughout its whole mass, and at the outset, the heat stored up in the brickwork. To obviate this the pan of about 20 to 22 gallons capacity, generally of cast-iron, enamelled inside, is contracted in the middle and rounded at the base, so that the bottom only is exposed to the action of heat. Otherwise the process is conducted as before, only the oil is heated a little longer, say, 4 hours instead of 3. This pot is lifted off the fire on to an iron stand (Fig. 85) by two wrought-iron bars 7 to 10 feet long, passing through loops fixed to the side of the pot so that in case of fire the bearers may be at a safe distance, but mechanical arrangements are now used to lift and convey both oil-boiling pots and varnish pots from the fire. In oil-boiling by steam the oil may be run by gravitation into the boiled oil store tank, however far distant from the pan.

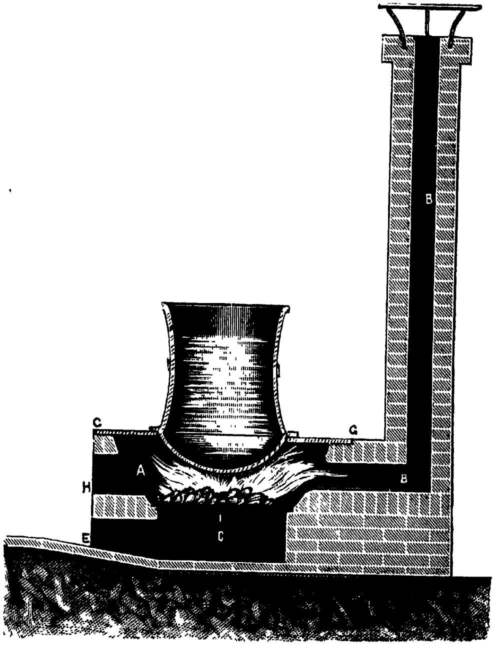


FIG. 84.—Portable oil-boiling pot. A, B, flue and chimney-stalk; C, plate on which flange of pot rests.

When large quantities of oil are to be boiled no good purpose is served by multiplying operations. It is better to use larger pans. In an extensive business the pans may measure 6 feet 6 inches high by 5 feet in diameter. Nevertheless we more often meet with pans having a capacity of 60 to 120 gallons. In fact big pots in oil-boiling by fire are clumsy, dangerous, and expensive in working and in handling the boiled oil. The pan is of strong iron plate about ⅙ of an inch thick, is built into masonry in such a manner that the upper part controls a circular gutter of 1½ to 2 inches deep, which, in case of the oil boiling over, conducts it to an adjacent receiver. The pan can be so built into the brickwork that it may be heated on part of its bottom and its sides, or, on the contrary, and preferably, on its sides alone. In the first case it so rests on the brickwork that the centre part of the bottom is exposed; in the second case, so as not to overheat the bottom part, it is supported by a small arch of brickwork, thus preventing solid matters from tenaciously adhering to the bottom. The *cylindrical* form of pan is not always adopted. We often come across pans almost *conical* in shape, the narrow part of which forms the bottom—a form which has the advantage of distributing the heat more evenly, and, owing to the larger section, of diminishing, in case of frothing, the chances of the oil running over. Such a pan is half or at the most two-thirds filled with oil and at first heated gently, and when the oil reaches 100° C. (212° F.) the impurities on the surface are skimmed off. The driers, previously completely desiccated and ground very finely, are then added. It would not do to add them in the beginning, as they would fall to the bottom, and their effect be to a great extent lost. Andés gives the following proportion for 20 gallons of oil:—

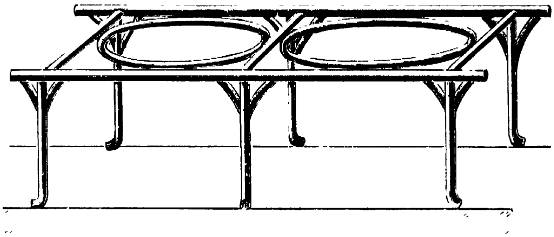


FIG. 85.—Iron stand (double) for holding pot shown in Fig. 84, after removal from fire.

2¾ lb. red lead, 2⅛ lb. litharge; or
2⅛ lb. litharge, 2⅛ lb. sugar of lead; or
1⅞ lb. borate of manganese; or
2⅛ lb. hydrate of manganese.

Boiling is kept up for 5 hours not exceeding 220° C. (396° F.). The temperature is regulated by means of a thermometer in metal

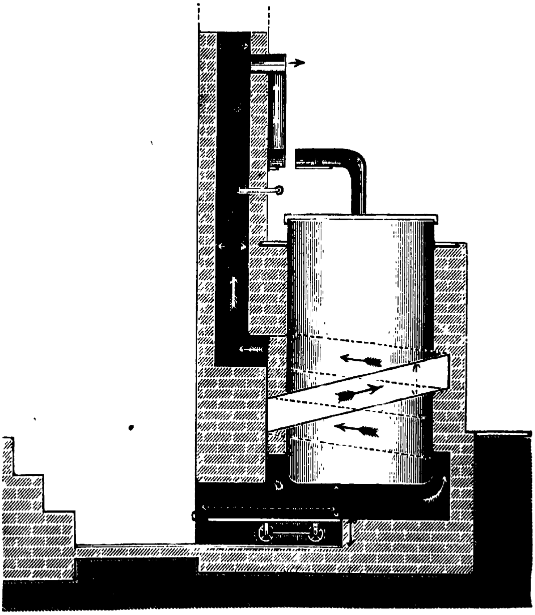


FIG. 86.—Plant for oil-boiling by naked fire (*with removable grate running on rails*)

framework, or, better still, by an aneroid thermometer, which is more legible, and not so fragile. Formerly the heat was occasionally regulated by adding some tin. The degree of heat was at one time

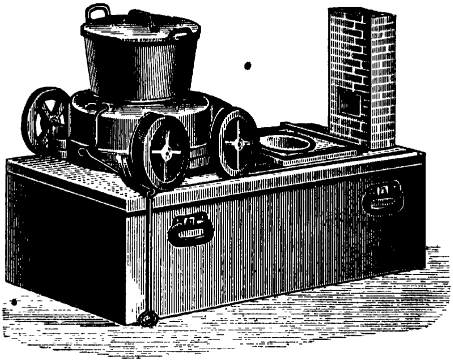
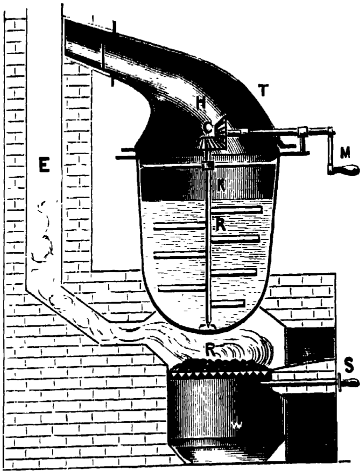


FIG. 87.—Oil-boiling by fire. Movable furnace and portable oil-boiling pan.

ascertained by dipping the quill end of a feather, which ought to at once shrivel and curl up, into the oil. This is still a handy test although the ultra scientific may sneer at it. The more attention there is paid to ensure a constant regulated temperature, the brighter and paler will be the oil. When very quick-drying properties are aimed at the oil is boiled from 1 to 2 hours longer, and the amount of driers increased from 20 to 25 per cent. At the time of adding the driers the oil should be well stirred either with an iron spatula, or preferably by means of mechanical agitators (a revolving shaft with arms, or a simple hanging chain fixed at both ends to a horizontal shaft, bent twice at right angles, fixed above the pan; the chain descends almost to the bottom of the pan and is turned by means of a crank some distance away). A wood charcoal fire allows a constant temperature to be maintained if the fire be well regulated. Coke will suit equally well. So as to lessen the risk of the temperature rising too suddenly, which would colour the oil and cause it to overflow or aggravate the risk of fire, it has been suggested to use a movable grate, which can be lowered instantaneously, and thus cause the fuel to fall into a pit full of water (see Fig. 86). Movable car furnaces running upon rails (Fig. 87), and thus capable of being easily removed, have also been employed. Oil is sometimes boiled by immersing the pan in a sand-bath, or in a bath of a suitable alloy. But this plan is hardly to be recommended, because if the temperature rises too high, the oil cannot be withdrawn from the source of heat; the same thing sometimes happens when the pan is built into masonry or set in brickwork, for even in the case of a movable furnace the oil remains exposed to the action of the heat stored up in the brickwork. To remedy this the pan, which sometimes measures more than 9 cubic feet, is mounted on a kind of trolley. The circular opening of the fire is level with the ground. If the temperature rises too high the trolley supporting the pan is removed from the fire; a movable hood with counterpoise descends over the top of the pan and carries away the fumes. This enables the oil-boiler or varnish-maker to watch the operation very easily, and preserves the metal of the pan. When the operation is terminated the oil is ladled out, and on the large scale pumped into a galvanised iron tank. As soon as the pan is empty it is immediately recharged with another batch, and generally without being cleaned in any way. The coating which forms on the sides of the pan prevents the oil from darkening, but care must be taken to remove any excess of driers from the bottom of the pan, otherwise unintentionally an excess of driers, which might have an injurious effect, may be added to the next batch. When the skin becomes too thick it is scraped off. In certain factories this is only done once a year, or once in 2 years. The foots from oil-boiling by fire may be used in making black paints, which are so difficult to dry.

In Dullo's process 250 kilos. of oil, to which 7½ lb. of black oxide of manganese and the same quantity of hydrochloric acid have been added, are heated in a copper boiler without reaching the boiling-point. This is stirred up with a spatula covered with a sheet of zinc. The operation is finished at the end of a quarter of an hour; by prolonging it the varnish has greater drying power, but becomes more and more coloured. After remaining 24 hours the oil is decanted, and is limpid and fluid. The deposit is used to make glaziers' putty.

In Barruel and Jean's process from 100 to 130 grammes of chemically pure manganese borate are ground up with 2 kilos. of old clarified linseed oil. The mixture is heated for a quarter of an hour almost to the point of ebullition. The manganese salt dissolves and the oil takes a chestnut-brown colour. The product dries in 24 hours.



. 88.—K, oil-boiling pan, with fire-quenching arrangement; R, agitator with blades; M, crank-handle working cog-wheel gearing, C; H, hood to convey fumes to chimney-stalk, E; R, hearth, the bars of which are kept in position by the rod S, by means of which, if the oil threatens to prime over or catch fire, the furnace may be extinguished by tilting its contents into the vessel W, filled with water.

Boiled oils prepared with manganese and lead oxides dry slowly and do not give a hard varnish. The manganese driers give much the best results. As for litharge, it is the drier with a lead base which gives the best results—the oil dries quickly and the coat is hard. When the boiling has not been done at too high a temperature the oil is hardly coloured. Acetate of zinc is the drier to be preferred amongst those with a zinc base. The borate and the citrate also give good results. Manganese borate and the acetate of manganese are the best driers with this base, the borate being the better of the two When the acetate is employed the oil must not be heated much above 230° C., otherwise it will take a dark colour, due probably to the formation of tarry products. The chlorides, nitrates, and sulphates are not good driers. The first two are too violent in their action, whereas the last are difficult to decompose and require too high a temperature. No advantage seems to accrue from the employment of the formates, citrates, and tartrates.

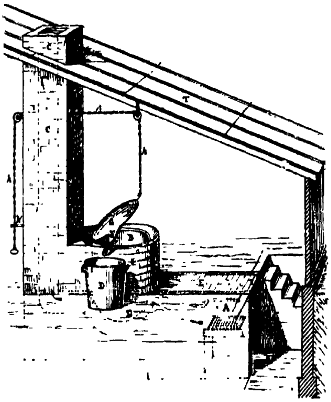


FIG. 89.—Oil-boiling by naked fire. Tripier-Devaux process. General view.

The Preparation of Boiled Oil for Enamelled Leather.—According to Andés, the so-called blue varnish applied to primed leather, for the purpose of imparting thereto a blue-black tone, deep brown in colour, and only becomes blue-black on drying. This process is analogous to the operation in carriage varnishing, wherein a thin transparent coating of Prussian blue lacquer is applied to the black surface in order to neutralise the greenish tone produced by the finishing varnish. Blue varnish, when dried on a metal surface at a temperature of 80° to 90° C., gives a highly elastic coating that will even stand hammering. The linseed oil used must be of good quality and free from mucilage when heated to 240° to 300° C. After heating to this

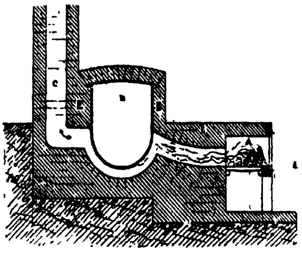


FIG. 90.—Oil-boiling by naked fire. Tripier-Devaux process. Longitudinal section.

temperature and recooling to 130° C., it is mixed with 10 per cent. of Prussian blue (ground fine and made into a paste with linseed oil), the whole being stirred and heated until it froths up. The heating of the mass is then continued with great care, until it thickens and turns from blue to brown, the proper thickness being attained when a rapidly cooled sample can be drawn out in long threads between the fingers. The finished varnish is left to cool slowly, so as to allow the undissolved blue, etc., to settle down, the supernatant varnish being filtered, and the sediment used up in the next batch. Wiederhold found that the sediment in the pots consists of a resin (soluble in oil of turpentine) formed from the linseed oil employed. For use, the varnish is thinned down with oil of turpentine, driers being added if drying is to proceed at the ordinary temperature. Nitric acid is also used in the preparation of blue varnish, being a powerful oxidising agent; but its use is to be deprecated owing to the difficulties in the purification process. More complex formulæ than the foregoing are sometimes used. For instance, 550 parts of linseed oil, 3 of lead acetate, and 1 of anhydrous zinc sulphate are heated together at 200° C. until viscous, then mixed with 27½ parts of Prussian blue, 10½ of umber, 3 of Frankfurt black, 3 of manganese dioxide, 6 of litharge, 6 of ferric oxide, 3 of manganese borate, 3 of brown shellac, 2 of dammar, 2½ of molten amber, 2½ of sandarac, and heated for several hours at 200° C. before thinning down with turps. Mohr has introduced a method in which 1½ parts of ferric chloride and equal quantities of ferrous sulphate and potassium ferrocyanide are intimately mixed, moistened with nitric acid, and dried by heat. Meanwhile, 100 parts of linseed oil are boiled for a couple of hours, and then mixed with the above preparation, the whole being incorporated with ⅙ part ot tallow that has been allowed to grow rancid in moist air, 1 part of green earthy pigment, 1 of puzzolane earth, and 1 of infusorial earth.

Villon's Method.—The oil after boiling is tanked from 15 to 20 days, then run back into the pot, heated up to 100° C. (212° F.), and 1 lb. finely ground bichrome added in five portions. It is kept at this heat for quarter of an hour, then the heat is increased up to 160° C. (320° F.) and kept at that for an hour. Prussian blue, 1 lb. for every 10 lb. of oil (finely powdered and sifted through silk) is sifted on to the oil through an iron sieve. The heat is steadily raised until after 3 hours it reaches 250° or 300° C. (482° to 572° F.). Much inflammable, bad-smelling, irritating fumes are given off during the process, so that the pot should be covered with a hood in the form of a still head to carry away these fumes. A mechanical stirrer keeps the mass in motion. Whilst the blue-boiled oil has been in preparation, another mixture has been in preparation in an autoclave, viz. linseed oil 100 lb., copal 100 lb., shellac 100 lb., turpentine 300 lb. This is kept at 350° C. for half an hour, 30 per cent. of this varnish is mixed with the hot oil. A sample of the substance when spread on a glass plate and cooled should form a deep brown shining coat without any stringiness or oily edge.

Another Formula.—400 lb. oil are heated to 100° C. (212 F.) then 2 lb. of bichromate added. The heat is increased to 160° F., and 40 lb. of Prussian blue added. The heat is increased so as to reach in 3 hours 250° to 300° C. (482° to 572° F.). On the other hand, 25 lb. of linseed oil, 35 lb. of copal, 75 lb. of Venice turpentine, and 7 parts of ceresin are heated to 350° C. (662° F.). The two solutions are mixed and thinned with turps.

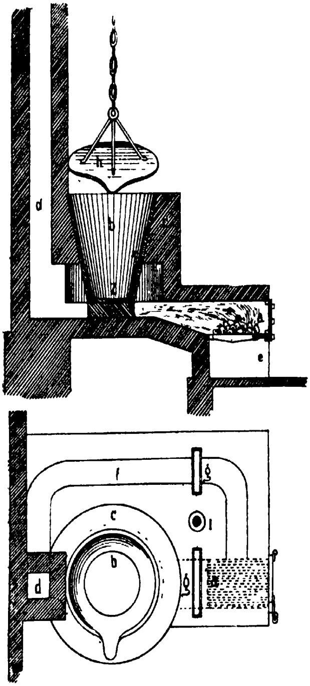


FIG. 91.

Fire Risks and Prevention of Nuisance.—During boiling, pungent, inflammable vapours are emitted. Working with small quantities of oil, all that is generally deemed necessary to prevent fire is to have a cover at hand to place on the pot should the necessity arise. On the large scale, when the oil is heated in a pan, a hinged lid is fixed over the pan during the boiling by means of a cord. If the oil takes fire the cord burns, and the cover falls automatically on to the pan. Different arrangements have been adopted so as to mitigate the fumes. On the small scale, a simple hood connecting with a chimney-stalk of sufficient elevation and draught is placed above the pot. A better plan is to fix a sheet-iron lid or dome above the pot (Fig. 91), provided with an opening by which the process may be watched, or the contents of the pot stirred. The cap is connected by means of a pipe with a tall chimney-shaft, the lower part of which is closed by a plug. Here thick viscous products with a vile odour condense. They are removed from time to time by opening the plug. The more volatile products escape from the chimney-top. It is, however, better not to allow fumes to so escape, and this may be effected by causing them to pass through a condenser which may be in connection with the chimney. A very simple way is to cover the boiling-pot with a movable lid provided with a "window" in the centre to easily open so as to permit stirring of contents. On the side is a disengagement tube, which can be luted to a pipe connected with a condenser. The latter may be a pipe, shaped like an organ pipe, leading into a vessel containing water, or it may consist of a vertical cylinder, the interior of which contains a coil of piping, through which cold water circulates. The vapour passes through the space *not* occupied by the pipes, and is in a great measure condensed. The advantage of this is that the wide, straight cylinder is not so liable to get choked up. It is advisable to use an aspirator because the vapours are heavy; by working with one or other of these arrangements condensation is almost complete. If need be, the uncondensable vapours may be led through a fire to burn them, as shown. Often no condensation is attempted, and the fumes are led directly into the fire. The large quantity of air which is mixed with the fumes does away with any danger. It is, however, necessary to be careful that the oil in the pan does not catch fire when these products are conveyed directly to the fire which heats the pan, or to a special furnace. The oil may take fire by the heavy vapours condensing in the pipe almost as soon as they leave the pan, and should there be any flaw they may run slowly backwards towards the fire and there become inflamed, and thus heat to redness the connecting pipe, which is generally of sheet iron, and thereby set fire to the condensed products in proximity to the boiling oil, and thus to the oil itself. This is easily remedied by protecting the lower part of the conduit pipe by fire-clay bricks, and adding a damper, so that communication may be shut off should the temperature rise too high. If the fumes be condensed by means of a properly constructed condenser between the pan and the fire, no fear need be entertained.

Oil-boiling by Steam.—There are two great drawbacks, viz. danger of fire and the dark tint which the oil assumes in contact with overheated surfaces. It has been tried to remedy these by boiling oil by steam heat, and ensure perfect safety, economy, and rapidity, advantages the more to be appreciated because this method produces pale oils. The simplest plan is to heat oil in a pan by *steam coil.* Steam at about 4 to 5 atmospheres (60 to 75 lb. pressure) is passed through the coil so as to heat the oil to about 150° C. (302° F.), but a much lower temperature, about 40 lb. steam, may be employed. A mechanical agitator spreads heat uniformly through the bulk of the oil. Working with a pan capable of holding half a ton of oil, when oil has been heated for ½ hour the necessary driers are added, and boiling continued for 6 hours, the mechanical agitator being kept at work all the time. The process is, says Livache, rendered more economical by using superheated steam. The steam before entering the pan passes through a coil in a furnace capable of bringing it to 400° C. (752° F.). When the superheated steam in its passage through the coil in the pan has brought the oil to the desired temperature, it is then only necessary to maintain it at that temperature by means of the steam admission valve. But there is no necessity for this superheating, 40 lb. steam does all that is required. It is not intended to distil the oil, and unless this were so there is no reason for superheating. To work as economically as possible, the gases evolved from the furnace in which the steam was superheated are led underneath the pan and burnt to assist in heating the oil. But if this be economical, it introduces the element of danger from fire, the obviating of which we had, amongst other advantages, in view when adopting the process of oil-boiling by steam. In boiling oil by a steam coil there is always a serious drawback in maintaining a uniform temperature throughout the mass even with continuous agitation. Effectual commingling of the oil and driers is impracticable; the latter settle to the bottom, and the coil of piping prevents the agitator from reaching them. Were it not for this drawback linseed oil could be very well boiled in a comparatively shallow, lead-lined, rectangular wooden tank lined with 6 or 7 lb. lead. This, however, could be easily got over by pumping in air through a perforated pipe laid down so that each coil thereof alternated with a coil of the closed steam pipe. This, in conjunction with the mechanical agitator, would effectually prevent the drier from settling at the bottom. By suitable mechanical arrangements a boiling pan made in this way would be equally effectual and cost less, not only originally but also for maintenance, than the costly wrought-iron or copper vessels now in vogue. But certain manufacturers deprecate the continuous stirring of the oil as likely to produce bad results. Andés obtained good results by using a steam-jacketed pan (Fig. 92), 85 gallons capacity, "made from strong iron plate, ⅛ inch in thickness, and able to stand a pressure of 4 or 5 atmospheres; it is provided with a safety valve, blow-off cock, and a tap to run off condensed water. About 40 gallons of oil are run into the pan, the steam turned on, and when the pressure is sufficient the blow-off cock is opened for a minute to allow the steam and air to escape; this is repeated several times, and the escape valve adjusted, so that only the small quantity of spent steam, the replacement of which by superheated steam is necessary to keep the pan and contents at the desired temperature, is allowed to escape. The condensed water is run off when necessary. The steam is regulated so as to keep the temperature between 125° and 132° C. (257 and 269·6° F.), and the process lasts from 5 to 6 hours, but by prolonging the boiling and using more driers better quality oil is obtained. If care be taken not to exceed 132° C. (269·6° F.) the resultant oil is pale and bright. To stimulate oxidation during the boiling process Andés fixes a mechanical agitator on the surface of the oil, which is propelled very slowly. The same driers are used as in boiling oil by fire, but it is advantageous to alter the proportions. Only half of the quantities of lead compounds should be used, but double the quantities when working exclusively with hydrated oxide of manganese or manganese salts. To economise, two steam pans may be wrought together, the steam passing from the steam-jacket of the one to that of the other. But it is perhaps more advisable to utilise the waste steam so as to heat in an intermediate tank the next batch of oil as it comes from the settling tanks, and previous to the actual boiling. This preliminary warming almost does away with the frothing of East Indian linseed oil, and the consequent liability of the oil to prime over into the condenser when it is heated in the jacketed pan in the usual way.

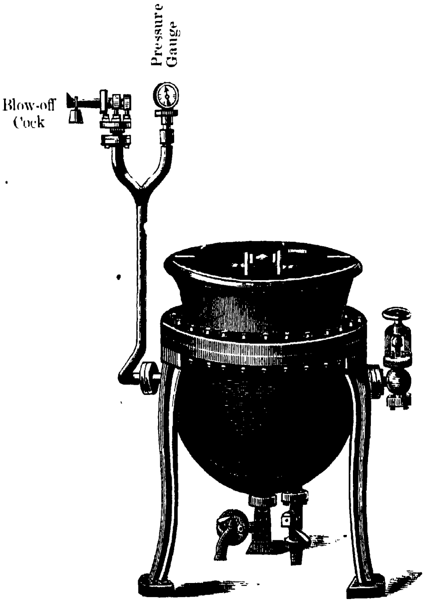


Fig. 92.—Steam-jacketed pan for oil-boiling fitted with blow-off cock and pressure gauge. This pan has the great defect of apparently not being provided with a fume condenser.

Vincent's Process for Oil-boiling by Steam with Simultaneous Injection of Air.—In Vincent's process a pan, preferably of copper, is used—having a depth equal to its diameter, of 2 to 10 tons capacity, and surrounded with a steam-jacket E, up to three-quarters of its depth, or to the oil level or a little above it, and capable of withstanding a working pressure of 40 lb. to the square inch—into the interior of which the steam is led, as a source of heat, and so regulated as to register throughout the process a pressure within the jacket of 35 lb. to the square inch. The top of the pan is closed by a dome riveted to it, and pierced with a manhole. In the centre is a stuffing-box through which pass two concentric vertical shafts—a hollow shaft encircling a solid one—armed with blades. By means of exterior gearing (Fig. 95 B) these fans turn in opposite directions, and in so doing intersect each other, and thus by their "dashing and cutting" action cause energetic agitation of the oil and thorough incorporation therewith of the driers. From the dome the fumes are either led by a 6-inch pipe to a condenser or into the furnace for heating the steam boiler. Finally, as soon as the pressure of steam on the pan registers 35 lb. to the sq. inch, equal to a temperature of 126·8° C. (260° F.), air is injected under pressure by means of a pipe passing through the jacket into the bottom of the pan. The oil to be boiled at one operation is first pumped into a large reservoir where it is stored as long as possible; from this reservoir it is run

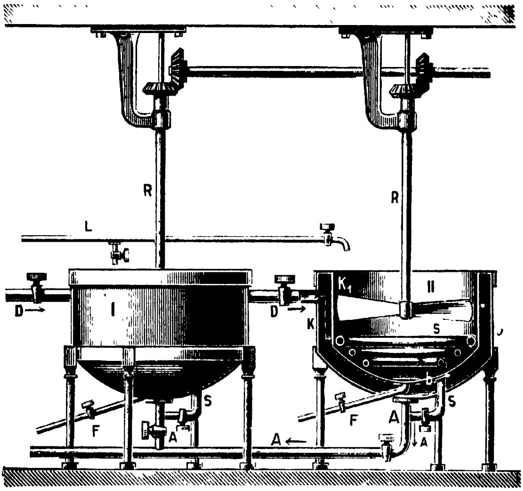


FIG. 93.—Steam oil-boiling pans, showing how to connect up series from same steam supply pipes; I., exterior view; II., section; R, agitator; KK_1, steam jacket; S, steam coil; L, raw oil charging pipe; FF, boiled oil discharging pipes; DD, steam inlet pipes; SA, condensed water and waste steam exits.

into an intermediate tank, traversed by a 1½-inch coil of iron piping through which the waste steam from the pan passes, thereby economising expense besides facilitating the deposition of impurities. The oil heated to about 35° C. (95° F.) is pumped or run by gravitation into the pan, and steam turned on in the jacket. As soon as the pressure marks 2 atmospheres, 35 lb. to the sq. inch, the agitators are put in motion and air pumped in. The finely pulverised drier, beaten up with a little oil to the consistency of treacle, is fed into the pan slowly and in a thin stream through a funnel with a stop-cock fixed in the dome as soon as the oil in the pan has become evenly and thoroughly heated through its bulk, or about ½ hour after the steam indicates a pressure of 35 lb. Introducing the drier in this highly comminuted condition prevents coagulation, and gives practical effect by complete diffusion through the oil to Vincent's theory of oil boiling by steam, which requires

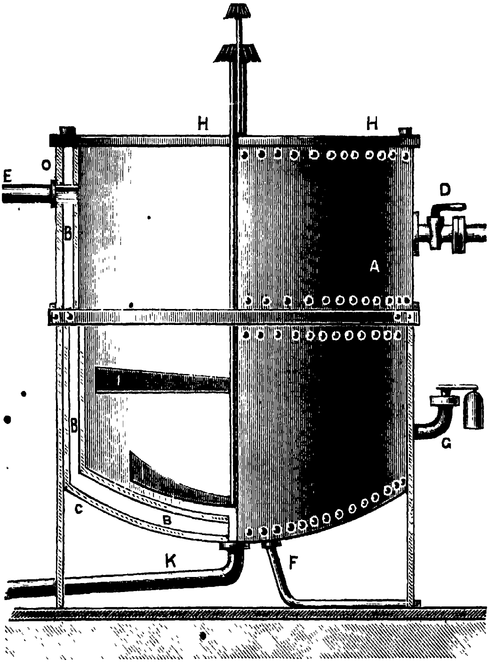


FIG. 94.—Steam-jacketed pan with agitator for oil-boiling, etc., fitted with safety valve. A, body of pan; BBB, steam jacket; C, bomb-shaped bottom; D, blow-off cock; E, oil entrance; F, waste steam and condensed water exit; HH, cover; K, boiled oil exit. Both K and F are fitted with turncocks, not shown. The pan is also fitted with a pressure gauge.

each particle of oil to be in contact with, or in proximity to, a particle of the drier used and the oxygen of the air at the same time. Air is injected in this way so long as it is absorbed and does not cause the oil to froth up and prime over into the condenser. It was thought at first it might be advisable to heat the air before injecting it into the pan, but this would appear to be useless, as it becomes so heated by the pressure to which it is subjected in overcoming the weight of the oil, lifting the heavy valves, etc., that the pipes through which it passes cannot be held in a firm grip in the hand, and not only so, but its passage through the oil cools the latter but very little. The process lasts 4 hours. By means of a 2-inch pipe in the bottom of the pan the oil is run into tanks where it deposits any undissolved driers, etc. It is through this discharge pipe that the air is injected into the oil. Injecting it in any other way leads to the injection pipe getting choked up with oil-skins, etc. Boiling oil by Vincent's process is especially applicable for use with the rosinates and linoleates of manganese. Vincent left us no record of the drier he used, possibly it was the borate of manganese; but the solution given under manganese acetate is an excellent drier for use in this process in the proportions stated.

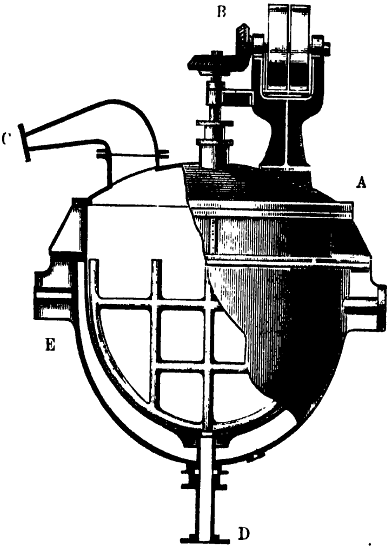


FIG. 95.—Oil-boiling by jacketed pan with dome, A, fitted with agitator driven by cog-wheel gearing, B, and pipe, C, leading to condenser; D, discharge pipe. It was through this pipe that Vincent injected air into the oil, but his pan was no doubt better adapted for this being done than the one shown in this figure.

The pans for oil-boiling by steam, as constructed by Greenwood & Batley of Leeds, are made from Siemen's steel-boiler plates, and are

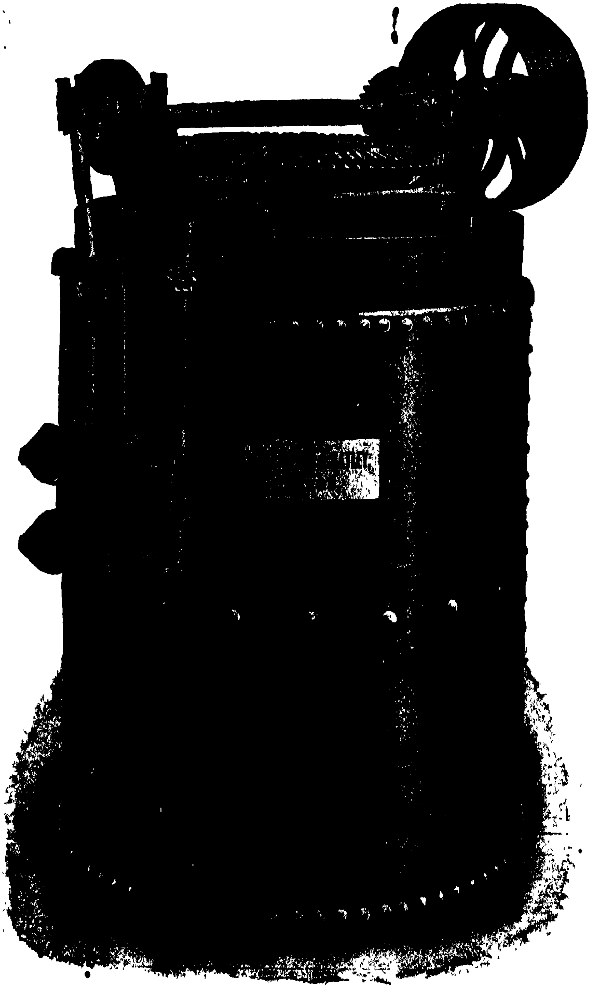


FIG. 96.—Oil-boiling pan heated by steam jacket, fitted with agitator and appliances for blowing the oil during boiling.

steam-jacketed round the sides and bottoms. They are constructe for a working pressure of 100 lb. per sq. inch, and tested hydraulic pressure up to 150 lb. before despatch from the work

Each pan is fitted with the following accessories, viz. blowing appliance in the shape of improved double-acting air pump with metallic air valve, and perforated air pipe leading to the inside of boiling pan. By the use of the metallic air valve all risk of stoppage is avoided, as compared with the ordinary class of pumps, which are fitted with leather or india-rubber valves, or by internal agitator working with the double-acting air pump for ensuring the chemicals being thoroughly mixed with the oil during the process of boiling. Self-contained belt driving gear for actuating the double-acting air pump and agitator. The above is arranged to be driven from any existing shaft, and the necessary steam for boiling is obtained from the main boiler of the manufactory, where the boiling pan is fixed. Other fittings are steam pressure gauge, gun-metal steam and drain valves, and main draw off tap with branch pipe.

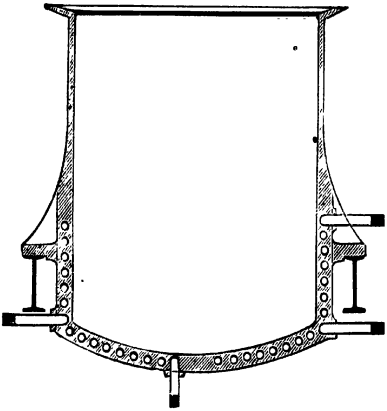


FIG. 97.—Patent boiling vessel.

Steam-heat Oil-boiling.—This new construction is most suitable for the employment of steam at any pressure, but it is especially intended to remedy the inconveniences arising in heating, melting, or evaporating such materials of which the boiling- or melting-point is higher than 200°. With many of the arrangements employed till now, it is almost impossible to prevent these materials from burning or igniting. To apply overheated steam direct to the material is for chemical or physical reasons in many cases impracticable. An indirect heating with overheated steam becomes expensive because sufficient heat can be gained only if the steam passes through quickly. If the overheated steam is allowed to stagnate in the heating pipes, the transference of heat is insufficient on account of its little specific heat. Moreover, the boiling vessels always require to have smooth walls because of the emptying and cleaning, and serpentine pipes must not be put in because they would hinder or even prevent the stirring of a liquid. With the patent boiling vessel all inconveniences are claimed to be removed; it affords great safety in working, and permits of special arrangements suitable to all branches of industry. The peculiarity of this boiling vessel consists in wrought-iron serpentine pipes of great strength (for instance, Perkins' pipes), being cast in its massive metal walls so that the heat introduced into the pipes is rapidly communicated to the well-conducting walls of the vessel which surround them, thus reaching the contents of the vessel. The inside walls of the vessel are smooth. The outside walls are protected against radiation by a heat-protecting coating. The pressure of the heating medium, for example, steam or hot water, is completely absorbed by the thick-walled Perkins' pipes, the walls of the vessel being consequently entirely free from pressure. The vessels may be provided with arrangements required for either purpose, such as stirring apparatus, steam dome, etc.

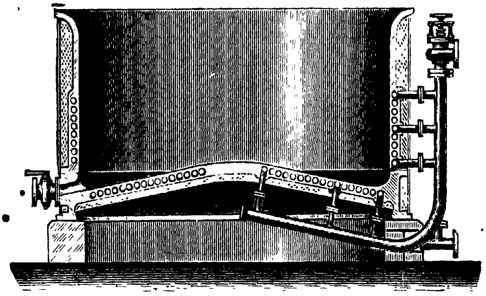


FIG. 98.—Oil-boiling pan fitted with pipes for superheated steam, air, or water, the pipes being fixed in the sides and bottom during casting.

Boiling by Superheated Air.—Notwithstanding the advantages of oil-boiling by steam, there is one drawback which has been considered so serious by some manufacturers as to lead them to give up this method. Even with superheated and thoroughly dried steam there was always a certain amount of moisture which acted on the metal of the pan, piercing it in holes and causing bursting or explosions. Superheated air was therefore substituted for superheated steam. This air is drawn by a fan from the superheater to the (steam) coil or jacket, and is again returned to the superheater, thus working in a continuous cycle. The difference between the specific heat of steam and that of air renders the economy of the hot-air process very problematical. The coil in the pan is of copper, which, although dearer than an iron one, does not colour the oil. As copper is also attacked by hot oil, it has been recommended to electro-plate it with silver. The coating need only be but very thin, as it undergoes no wear and tear.

Rules for, and Changes which take Place in, Oil-boiling.—Three points require attention: (1) The amount and nature of the driers; (2) the temperature of boiling, and (3) its duration. When working with naked fire, the quantity of drier varies from 2 to 4 per cent. of lead compounds and 1 to 2 per cent. of hydrated oxide of manganese. The deposit which forms at the bottom of the pan consists of a viscous mud, and when a drier with a lead base has been used, we also find a notable quantity of *metallic* lead, whilst the boiled oil itself only contains about 1 per cent. of *oxide* of lead. It follows: (1) That the oxidisable principles of the oil have reduced a certain

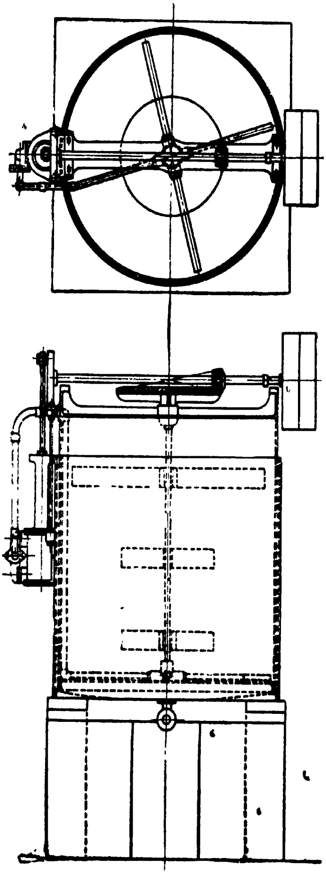


FIG. 99.—The Craig extractor for extracting oils, fats, etc. Section of linseed oil boiler (A. F. Craig & Co., Ltd., Paisley).

quantity of oxide of lead; (2) that a certain quantity of oxide of lead is thrown down in the form of lead salts insoluble in oil; (3) that a part of the oxide of lead enters into a soluble combination with the oil; this combination takes place by the simple saponification of certain glycerides of the oil, and consequently a corresponding quantity of glycerine is liberated. These different reactions are set up from the commencement at a moderate temperature. When manganese is used instead of lead, the boiled oil contains about ½ per cent. of oxide of manganese.

The temperature ought to be regulated between 210° and 228° C. (410° to 442·4° F.) so as to get a good boiled oil, because (1) oil when heated commences to give off volatile products at about 230° to 236° C. (446° to 456·8° F.), with the formation of fatty acids which yield oxidation products of inferior quality, requiring longer time to dry. When it is required to produce a limpid oil with but little body (which is not always the case; take printers' ink, for example), it is advisable not to go beyond 230° C. (446° F.). (2) Again, as a consequence of the saponification of a small quantity of oil a corresponding quantity of glycerine is liberated; now if this glycerine remained, in the free state, in the oil the oxidation products would never dry perfectly but remain tacky. The glycerine must therefore be eliminated; this result is obtained by prolonged boiling, for the glycerine is partially carried away by the volatilisation of certain principles of the oil, which are given off in small proportion during the whole process, however carefully regulated, and even although the temperature remains lower than the temperature of distillation of glycerine. Another portion of the glycerine decomposes under the action of prolonged heat, either in presence of metallic lead, as found at the end of the operation, or into volatile products such as acrolein, acrylic, formic, or acetic acids, and finally the larger quantity reacts upon the triglycerides of the oil, forming diglycerides which afterwards oxidise and dry perfectly. Now this latter reaction in which 1 molecule of free glycerine combines with 1 molecule of a triglyceride to form 2 molecules of a diglyceride, says Livache, occurs at 200° C. (392° F.), and to get good results, therefore, the temperature should not get below 200° C. (392° F.) nor rise to 230° C. (446° F.). A temperature of 220° and 228° C. (428° to 442·4° F.) is aimed at. Finally, the process lasts from 3 to 6 hours according to the size and shape of the pan, and the manner in which the furnace is built on which the pan is heated. The oil ought to be boiled long enough for the above reactions to occur, but the boiled oil finally obtained is better in quality the longer it has been boiled, for on prolonged boiling a polymerisation of the glycerides takes place, giving a final product which oxidises more rapidly and is very elastic after drying. According to Livache, this is the reason why in England, instead of boiling rapidly so as to "break" the oil as in France, the operation is carried on very slowly at the lowest possible temperature, the boiling proceeding for several days, sometimes for even a week. But, as already mentioned, the fire boiling of oil is long out of date in Britain.

When oil is boiled by superheated steam, or superheated air, the temperature is regulated between 125° and 130° C. (257° to 266° F.). The latter is superheated to 4 or 5 atmospheres, relaxing in the steam coil or jacket to about 2 atmospheres. It will be readily understood, looking at the matter from the double point of view of safety and economy, how difficult it would be to superheat the steam to such a temperature that the steam in the coil or the jacket would be at 200° C. (392° F.), because it would be necessary to heat the oil to 15 atmospheres. Consequently the liberated glycerine remains to a larger extent in the oil, and thus prevents it from drying so well as fire-boiled oil. However, as the oil boiled in this way is very pale, endeavours have been made to get over the difficulty, either by using a larger proportion of manganese drier, so as to have a more energetic oxidation and thereby a splitting up of the glycerine, or, preferably, by producing direct oxidation by a current of hot air, or finally, by causing a current of air to circulate through the whole mass of heated oil, or by projecting on the surface of the oil a small quantity of water so as to carry away the glycerine in its train. However this may be, it is most likely the reason why many persons prefer oil boiled by fire-heat. Nevertheless, prolonged boiling by steam diminishes and even abolishes this drawback.

Clarification of Boiled Oil.—When boiling is finished the oil contains (1) suspended solid matter, (2) coagulated or carbonised organic matter, (3) insoluble salts, (4) undecomposed or unreduced drier, etc. To hasten deposition the oil should be left at rest as hot as possible, because it is then more fluid and limpid, thus facilitating the more rapid deposition of extraneous matter. It should therefore be run from the boiling pan into the settling tanks as soon as the steam is turned off the pan. Working with small pans which can be easily handled, all that has to be done is to lift them off the fire and to let them stand for 8 days at least. But when working with large-sized pans built in masonry, they must be emptied quickly, by a ladle or by a pump, as hot as possible, into a reservoir of the same size, where it is left to deposit for a fortnight at least. There need be no difficulty in drawing hot oil from one vessel at a certain level to another vessel at a lower level by means of a lead-pipe syphon, which should be perfectly dry and filled with *warm* oil and held in the hands by a piece of stout felt if it be desired to touch it after it is set. In setting it the charged syphon should be brought as close to the surface of the hot oil as possible before letting go, or the end of the syphon may be plugged up and the plug driven out after it has entered the oil. After standing for a fortnight the decanted oil may be sent into the market. If stored too long before being used, the oil, at first limpid, becomes cloudy, or at least dull, when knocked about in moving or transported in barrels. This is due to chemical changes, which supervene slowly throughout the mass. All that has to be done is to allow the oil to stand for a day or two after it has reached its destination, and to decant cautiously. The amount of deposit formed in this way should not exceed 1 to 2 per cent. of the oil. Some oil boilers, who ought to have known better, have been known to fill boiled oil into drums for despatch abroad after scarcely 24 hours' settling, and that after boiling with 10 per cent. of cotton-seed oil! It need scarcely be remarked that goods made in this way are liable to be returned, and orders lost never to be regained. When cotton-seed oil is cheaper than linseed oil it is sometimes attempted to boil it in the proportion of 10 to 20 per cent. with linseed oil. An oil produced in this way will never clarify, leaving altogether out of account its diminished drying properties. Its very questionable recommendation is that it is an excellent way of producing a superabundance of boiled-oil "foots". Cotton-seed oil is, in fact, only classified as a drying oil to fit in with the ideas of theoretical chemists, who would fain make practice and actual facts subservient to theory. They choose to ignore the fact that stearine abounds in cotton-seed oil, and that nothing will prevent the stearate of lead and manganese from continuously settling out *ad infinitum.*

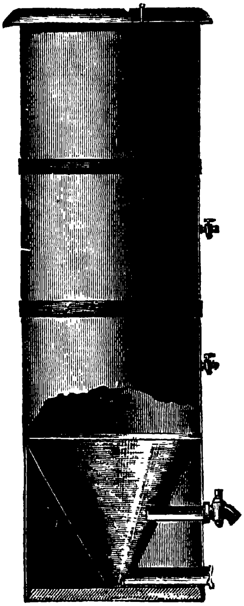


FIG. 100.—Clarification of oils by deposition. Tank for storing oil, showing conical arrangement for deposition of foots and draw-off cocks at different heights. (Donovan & Co., Ltd.)

The very prolonged storing of *boiled* oil, far from improving it, deteriorates it, especially in the case of lead-boiled oil. After from 5 to 10 years the oil separates into two fractions, the one solid and brittle, whilst the other, retaining its fluidity, can still be used. Oils containing manganese alone do not alter in this way.* The deposit formed during oil-boiling varies, according to the quality of the oil and the boiling process adopted, from 5 to 8 per cent. of the quantity of oil treated. It is of medium consistency, and, according to the quality of the oil, the colour varies from white to yellow. Andés states that impure, bad quality oil gives a white or yellow deposit, whilst well-purified good oil yields a brown one, with no granular or crystalline appearance. If the boiling process has been well conducted, i.e. at a temperature not exceeding 220° C., this deposit constitutes the only loss. It is carefully collected, being worth sometimes as much as 50 to 60 per cent. of the oil used. It finds a use in the manufacture of mastic (cements), soap and low-quality paints, especially low-quality blacks, the tint of which it does not injure, whilst it greatly improves their naturally bad drying properties. When rosin was cheap and rosin oil did not cost more than £5 a ton, the *loss in oil-boiling* and the cost were compensated by adding 2 or 3 per cent. of thick rosin-oil to the raw oil before boiling. This percentage does not affect the finished oil to any great extent.

Boiled Oil.—Boiled oil or oil prepared as just indicated is a very important factor in painting. However, in house decoration raw linseed oil is the vehicle used in painting. Raw linseed oil penetrates wood and that is supposed by many to be a virtue, whereas the impenetrability of wood to boiled oil is held by many to be one of its drawbacks. It is ground along with *white*, that is to say, white lead, so as to obtain a soft paste, which is thinned down in various proportions with linseed oil and spirits of turpentine until the desired fluidity is obtained. If a certain shade is desired, the colouring matter beaten up with a small quantity of oil is added; finally, if very rapid drying is required, what are known as "Patent Driers" (siccatives) are added. These may consist of (1) a solid powder (litharge, red lead, or zumatic, i.e. a mixture of oxide of zinc and borate of manganese); (2) litharge or manganese-boiled oil when there is no reason to fear the painting, or by a drying oil, the drying properties of which have been stimulated by appropriate treatment (precipitated lead, acetate of lead, etc.); or (3), finally, of special preparations, the base of which is oil known under the name of liquid driers, but which are only used with coloured pigments, as they turn white tints yellow. The paint so formed slowly changes when spread upon any surface in a thin layer to a solid body, which forms a protective coating against external influences. The paint ought not to dry too quickly, for the slower it dries the more it is capable of expanding, and thus lasting the longer. The fluidity ought to be such that the paint flows easily from the brush whilst at the same time it does not run in streams, but spreads out in a continuous homogeneous coating. The coating must also be thin enough to prevent the formation of pellicles at the surface, which would hinder the part underneath from drying. It is therefore advisable to apply several successive coats. But each of these ought to be allowed to dry thoroughly before the succeeding one is applied. With linseed oil substitutes, none of which can possibly form insoluble linoxin on drying, the second coat of paint is sure to disturb the first, especially if applied to outdoor work in warm weather, and if spirits of turpentine or thinners be added to hasten the drying. *Substitutes of all kinds should be avoided.* They give rise to more worry and annoyance than eventual economy. In some extreme instances one might as well apply methylated spirit to wood coated with brown hard spirit varnish as apply a second coating of these substitutes. In using boiled oil a brilliant coating is not aimed at, the question of appearance being subordinate to that of resistance and durability. It is preferable to impart brilliancy by a final coat of varnish. For the grinding of paints in oil, stiff and liquid, see J. Cruickshank Smith's *Manufacture of Paint* (Scott, Greenwood & Son).

Qualitative Test. Rosin in Boiled Oil.—As a qualitative test for purity of boiled oil Lippert recommends the Storch-Morawski reaction: 2 or 3 drops of boiled oil are dropped into ½-inch test tube, taking care not to come in contact with the sides, or the oil will char in the sulphuric acid afterwards added. About 1½ c.c. of glacial acetic acid is then poured in, well shaken up, and left to rest until most of the oil has collected on the surface, a little sulphuric acid (sp. gr. 1·53) is run down the sides of the tube, and collects at the bottom. At the contact zone between the two acids there forms a brown ring, which assumes different colours in the upper portion, and is rendered more prominent by gentle shaking. Pure boiled oil, containing lead or manganese oxide driers, boiled with the oil, gives a dark brown coloration, whereas rosinates or added fish oil or rosin oils, will give red to blue shades. Maize oil, said to be largely used as an adulterant of boiled oil in America, also gives a red coloration. A pure linseed oil, which gave no colour reaction, was boiled with an addition of rosin driers prepared by dissolving lead oxide and manganese hydrate in rosin, when the temperature attained 150° C. This latter, too, gave no colour reaction in the Storch-Morawski test, but the resulting boiled oil gave a beautiful blue colour in the acetic acid layer. High priced linseed oil has led to considerable adulteration with fish oils, a very large quantity of sardine oil having been exported from Spain for that purpose. Oils adulterated in this way were tested by the Storch-Morawski reaction, and mostly gave a violet coloration. Saponified and shaken up with water they all exhibited considerable turbidity; and when extracted with petroleum spirit furnished a thick oil of disagreeable odour, which (unlike rosin oil) was readily soluble in glacial acetic acid, and gave a beautiful red coloration under the Storch-Morawski test. This substance was analogous to that extracted from fish liver oil by Jean, and gave the same handsome purple colour reaction when treated with a drop of sulphuric acid, the acid turning red. The faculty of furnishing this colour reaction, however, disappears when the oil has been exposed to light for some considerable time; and a similar behaviour was observed in the above when stored in the light for a year. The actual presence of fish oil was also proved by the extraction of cetyl alcohol, melting at 50° C. In connection with the alleged drying properties of fish oils, it is mentioned that these oils when mixed with driers throw down a copious precipitate, and therefore render the dryers inoperative. Moreover, the paints prepared with such oils remain sticky for days, and have a muddy appearance, so that there does not seem to be any prospect for the adoption of fish oils as paint vehicles (Chem. Rev. Fett. u. Harz-Ind.).

Linseed Oil Substitutes.—The varnish-maker and oil boiler and paint grinder often require substitutes for raw materials which have risen in price, and also to change raw materials which have not risen, when painters can nevertheless no longer afford to use the products made with them.

The pale colour, somewhat thick consistency, and slight smell (when well made) of refined rosin oil (RRO) have naturally brought it to the front as a substitute for linseed oil when the latter is too dear. The objections that have been urged against rosin oil are that boiled oil in which it replaces part of the linseed oil will not answer with lead or zinc pigments, but make a hard cement-like mass after only a few days, that the coats easily turn yellow, do not dry properly, or only very slowly. The slow drying of rosin oil and linseed oil when boiled together cannot be remedied even by large quantities of liquid drier. This addition, too, greatly darkens the colour. It is true that good drying rosin oil is made in England, more especially in Scotland, and a few places elsewhere; but once it is mixed with linseed oil it loses its drying power to a great extent, and the varnish will dry no better than if inferior rosin oil had been used. To make ordinary refined rosin oil drying, it is heated by steam in shallow pans, and kept at about 130° C. for from 2 to 6 hours. From 3 to 5 per cent. of drier (borate or rosinate of manganese) is then added, and the same temperature is kept up for another hour. Of late, solutions of rosin in petroleum are added, together with the rosin oil, to the linseed oil. The rosin makes the result better, but does not improve the drying qualities. It is true that a mixture of good drying linseed oil, with not more than 25 per cent. of refined rosin oil (RRO), dries well, but it has the drawback of decomposing with lead pigments.

Pietzker, of Hamburg, makes rosin-oil varnish from fused rosin, with sulphites or hyposulphites as driers, and then dissolving the whole in the rosin oil. His process is to melt some rosin, dissolve resinate or lineolate of manganese, lead or copper in it, and then, when the temperature has fallen to 100° C. he adds a 20 to 40 per cent. hyposulphite of potash, lime, magnesia, lead, or zinc, or sulphite of potash, either dissolved or stirred up in water. The whole mass is carefully stirred, and kept at 100° C. till all the water is evaporated and the mass is quite limpid. The sulphur compounds are then allowed to sink to the bottom. Of the rosin thus prepared, from 5 to 20 per cent. are poured into hot rosin oil, in which from 3 to 5 per cent. of the above-mentioned rosinates or linoleates have been previously dissolved. The same result is attained by dissolving in rosin oil 5 to 15 per cent. of rosin and 5 per cent. of a linoleate or rosinate, and then adding 5 per cent. of the hyposulphites dissolved in water, and heating and stirring to get rid of all the water. A better process is as follows: From 3 to 5 per cent. of rosinate or linoleate of manganese or lead are dissolved in rosin oil. The solution is stirred up at 50° C. with a strong solution of a chlorate or chlorite. The mixture is then allowed to stand without cooling till the water and oil have separated, and the oil is quite clear and can be poured off.

Definition.—If the French equivalent for our boiled oil, *Huile cuite*, be readily recognisable, it is not so with the German equivalent, *Firniss*, which smacks too much of our "varnish". For over three decades the present author has been protesting most energetically against the German *Firniss* being rendered into English by incompetent and unfit technical translators as "varnish," but they are incorrigible. Mulder defined *Firniss* as including all substances which leave a shining dry surface, when a solution of a solid body in a fluid, which latter when applied as a film evaporates, leaving behind a shining elastic film—very apparently a false definition which applies both to our own oil varnish and to the German *Lack* and the French *Vernis*, and not at all to the German *Firniss*, nor to our own boiled linseed oil, nor to the French *Huile cuite*. Even German authorities themselves declare very positively it would be far better to define their *Firnisse* as *gekochtes leinöl*. In Germany this false definition of *Firnisse* is so general that Weger rightly describes it (*Firnisse*) as a linseed oil, heated to a high temperature and maintained thereat for some time. Lippert takes *Leinol firnisse* to mean a linseed oil containing lead or manganese. It has been a great drawback that both the English and French false rendering of the German *Firnisse* should be varnish and *Vernis* respectively, and not rendered truly as boiled oil and *Huile cuite*. This false rendering has been the cause of a continuous flow of most ridiculous technical ultra-stupid errors in fact for several decades. It has already been stated that linseed oil containing driers is termed boiled oil, which definition, be it well understood, is wholly and solely applicable to boiled linseed oil. There is no such thing on the market as a genuine sample of a boiled oil in a general sense other than linseed. The purchaser of boiled oil invariably means "boiled linseed oil". But this definition is regarded by some authorities as incomplete. Weger defines it thus: boiled oil (*Leinol firnisse*) is a linseed oil prepared with oxygen, or substances containing oxygen, which dries in the air, in a thin film in less than 24 hours. This definition was added to later on, and boiled oils were classified as (*a*) oxidised boiled oil, (*b*) linoleate boiled oil, and (*c*) rosinate boiled oil, by Lippert. In preparing boiled oil we are told that it varies in quality with the geographical source of the raw oil. Oil from Baltic seed is to be preferred to all others. A very good boiled oil is produced from the oil from Dutch and Morocco seed. Then follow (1) Indian, (2) S. Russian, (3) North American, and finally (4) La Plata seed. Both (*a*) soil and (*b*) climate influence the quality of the oil. A great value has been attached to old tanked linseed oil, i.e. oil that has been stored a long time, as being, in virtue of such storage, especially suitable for varnish-making. Numerous writers, including Wilson

Neil, from whom most of them have copied without acknowledgment, have prescribed that linseed oil for varnish-making should be stored 1 to 2 years.

Mulder gave the following instructions for preparing a good boiled oil: Linseed oil is boiled with 3 per cent. of red lead, with access of air for 2 hours—no temperature was prescribed—allowed to settle, and filtered. To finish, the boiled oil so obtained was sun-bleached, in lead-lined vessels. As far as the chemistry of oil-boiling was concerned, Mulder found that on heating linseed oil with lead oxides, at water-bath temperature, a certain amount of glycerine was split off, and that the corresponding quantity of lead went into solution as lead linoleate.

Saponification of Linseed Oil by Lead Oxide.—C. H. Hall believes that during the action of lead oxide on linseed oil partial saponification may occur, but that idea goes back beyond the memory of man. If litharge or red lead be mixed with linseed oil to form a paste, the latter with access of air becomes thicker and can be drawn out between the fingers. The cause cannot be alone ascribed to the formation of linoleate of lead, which only dissolves in linseed oil in the cold with very great difficulty to separate out afterwards, J. B. Hannay treats the question differently. He found that during the heating of linseed oil with litharge to 170° C. (338° F.), he only obtained glycerine-free water. From that he concluded that the lead oxide was distributed between the glycerine and the fatty acid, with formation of a plumbo-glyceric linoleate with the following formula :—

$$\begin{array}{l} CH_2 . O . Pb . O . CO . C_{17}H_{29} \\ \dot{C}H \;. O . Pb . O . CO . C_{17}H_{29} \\ \dot{C}H_2 . O . Pb . O . CO . C_{17}H_{29} \end{array}$$

Finally this lead glyceride plays an important rôle in drying. Many believe on very good grounds that oil-boiling consists in dissolving a certain amount of lead or manganese in the oil, amongst others Dr. Sabin of New York.

The Degree of Heat Used in Oil-boiling.—The necessity for oil-boiling has already been urged. Chevreul told us that oil heated to 70° C. (158° F.) for 8 hours dried better than oil heated to a high temperature. Mulder denied it. He heated linseed oil in a retort without any acceleration of the drying power; he also heated a linseed oil for ¾ hour and then boiled it for ½ hour with a similar result. However, he regarded the actual heating of linseed oil in oil-boiling as useful, as by its means his linoleic anhydride was prepared, which does not dry any further, and which in virtue of its rubber-like nature improves the film. It excludes air and volatile matter. It, however, is soft and does not cover well, therefore the paint does not set well. Weger later asserted that the temperature of oil-boiling does not affect the drying time of the oil, e.g. Weger heated a linseed oil for 3 hours with 3 per cent. of red lead to 200° C. (392° F.). The oil took 3 days to dry! with an oxygen number of 14·0, whilst linseed oil prepared from soluble driers solely in the cold dried in 4 hours. Be it well understood that 3 per cent. litharge would have given quite different results to 3 per cent of red lead.

Friend thickened Baltic linseed oil by heating (*a*) to 200° C. (392° F.) for 30 hours, (*b*) to about 300° C. (572° F.) for 36 hours, (*c*) to about 300° C. for about 42 hours without appreciable oxidation, with the result that (1) the coefficient of expansion steadily fell, (2) the density and viscosity rose with the temperature and length of treatment, (3) the molecular weight in benzene solution rose from 740 for the raw oil to 760, 1000, and 1420 respectively. A thin film of linseed oil when exposed to oxidation loses very appreciable quantities of water, CO_2, and organic vapours.[1] Maximum increase in weight merely coincides with a point of equilibrium at which the oxygen absorption counterbalances the loss due to escaping vapours, and there can be no ratio between the increase in weight. With a sample of pure Calcutta linseed oil during the various successive stages of oxidation the density of the oil gradually increased, the expansion coefficient fell, there being an increase in volume up to the setting point [*sic*] of the oil, after which the linoxin [*sic*] slowly contracted. The maximum increase in weight occurred after the oil had reached the setting point.[2] The expansion is dependent on the increase in weight so that the addition of certain substances to the oil which reduce the maximum increase in weight probably by facilitating the escape of volatile substances also reduces the expansion. The contraction suffered by linoxin on prolonged exposure to air explains the cracking of old paint.

Effect of Boiling Linseed Oil at a High Temperature.—The boiling of linseed oil at a high temperature is prejudicial, and with lead-boiled oils colour and hardness are injured. But if a linseed oil be heated without driers for 120 hours to 150° C. (302° F.), it is very long in drying, but very impervious and lustrous. It leaves a dark film.

Thick boiled oil is naturally difficult to apply in uniformly thin films. Fahrion applied three partially so-called polymerised [*sic*] linseed oils on tin plates, left them 10 days in the air, and determined the autoxidation products, viz. the oxyacids.

EFFECT OF PERCENTAGE OF OXYACIDS IN LINSEED OIL ON RAPIDITY OF DRYING.

	A.	B.	C.
Per cent. oxyacids, before . . .	0·5	4·4	7·6
,, ,, after . . .	30·6	20·8	16·4

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[1] ? Acrolein.—J. G. M.

[2] Both contraction and maximum increase in weight seem incompatible.

He concluded that boiled oil dries the better the less oxyacids it contains. This conclusion is not, he states, free from risk of error, as without doubt, in the case of B and C, the films were thicker and therefore the process was not complete in 10 days.

Lippert got for a stand oil with a steady rise, inner half 24 days, with oxygen number 9·6. To account for this low number he conjectured that during drying depolymerisation [*sic*] occurred.

Weger obtained in a much shorter time, but with more slender films, still higher numbers, viz. 18 days for a stand oil, 11·1; for a thickened oil, 10·7. The maximum weight occurs at the time of drying. The drying point is not sharp and is difficult to ascertain. A remark of Genthe's that linseed oil heated to 350° C. (672° F.) does not dry any more needs no contradiction. As Fahrion points out, in actual practice there is no over-boiled oil.

Does a Mucilaginous Oil Yield a Defective Boiled Oil?—Weger asserts that linseed oil mucilage in oil-boiling in nowise plays an important rôle, and mucilage-containing and mucilage-free oils gave, on the large scale, no difference in drying; the latter dried sometimes better, sometimes worse. Weger collected the coagulated mucilage or "foots" from a large quantity of oil on a filter, and tried, with little success, to free it from oil by draining through porous tiles. It then formed a yellowish gelatinous transparent mass, which still left very good films on glass plates, and in 3½ to 4½ days gave an oxygen number of 12·8 to 14·7. It has been urged that a previously demucilaginated oil is therefore not a desideratum, seeing raw oil is seldom used in oil-boiling, but is mostly bleached with fuller's-earth or sulphuric acid. But that is not correct. Oil so prepared is used as a vehicle for white colours, and every one of sound common sense will agree that Wilson Neil acted on the most sound principles conceivable when he freed linseed oil from mucilage by calcined magnesia, which if dearer than fuller's-earth is a much superior reagent for the purpose.

Weger's definition of boiled oil includes oil boiled without driers, but which has been treated with oxygen to produce previous oxidation. Hence linseed oil on blowing absorbs a known weight of oxygen and passes into linoxin quicker than raw oil. Prior to Mulder various opinions prevailed regarding previous oxidation. The oxygen of the air acted during oil-boiling by direct removal of the used-up vapours by the current of air (Webster). Against this Binks concluded to get a good boiled oil with 0·2 per cent. $MnSO_4$. 0·6 per cent. PbO should be warmed ½ hour at 60° C., and then a current of air blown through it, between 35 and 40° C., to thicken the oil and dissolve the drier.

According to Mulder, partial oxidation of the oil during boiling was due to the use of litharge. When red lead was used a partial oxidation with formation of lead linoxate occurred, also when air was excluded. Lead linoxate, writes Mulder, produces a hardening of the film, whilst by heating linseed oil with litharge, with exclusion of air, lead linoleate is formed. Finally, Mulder imagined this was confirmed by the following experiment: oil boiled with 2·6 per cent. PbO was mixed with 25 per cent. of white lead, and the mixture, spread on tin plate, exposed to the air.

Blown Oil.—The exact time when linseed oil was first blown during oil-boiling is unknown (C. Vincent, 1870). German literature is, as usual, probably in error historically when it states that blown oil came on the German market from England, and its use as boiled oil directly recognised. But Weger denies it is boiled oil. He found that with cold oil blown for 25 hours the oil neither thickened nor dried quicker, it absorbed little or no oxygen. On blowing the oil with the aid of heat the increase in weight in a thin layer begins sooner, and is much more rapid towards the end than is the case with the raw oil. But the rapidity of drying is not accelerated; thus if a linseed oil dries in 3 days with the oxygen number of 15·1, by blowing this oil on the large scale between 130° to 140° C. (266° to 284° F.), it likewise dried in 3 days with the oxygen number of 14·0. Both samples were 3 years old.

A raw Indian linseed oil dried in 6 days with the oxygen number of 16·8; the same oil blown for 25 hours at 250° C. (482° F.), and thus very viscous, dried in 6½ days with the oxygen absorption 9·3 per cent.

Steenberg's Researches on Blown Oils.—From these he concluded that the thicker the body of the oil the longer it took to dry. With the appearance of soluble driers, the blowing of boiled oil was said to come into vogue, but only during part of the time. But oil-blowing was very general before soluble driers, possibly it was borrowed from the lubricating oil industry or the linoleum industry. It simply consisted in blowing the oil for 1 hour at 120° to 150° C. In an example given by Weger the temperature was lower. A linseed oil with 2½ per cent. of lead manganese rosinate added to it in the cold, dried in 1½ days with the same oxygen absorption. Again, Dunlop and Sherk have shown that the iodine number of a long blown lead-manganese iled oil had sunk to 24·9.

Ozonised Oil.—An energetic method of making a more rapidly ying oil is partly due to the action of oxygen. Linseed oil treated th ozonised air for 2 to 3 hours increases in thickness and assumes the properties of boiled oil. Schrader and Dumoke tried a brief nisation. The reaction proceeds when linseed oil is placed in flat ins, especially in sunlight, which, moreover, acts of itself. The oil ches, thickens, and dries quicker. Sherry converted non-drying by ozone, using platinum black as catalyst, into drying oils. nes' electro boiled oil is prepared thus: A mixture of linseed s converted by a strong agitator into a permanent emulsion, and an electric current passed through it simultaneously. The decomposition of the water generates ozone, whilst the linseed oil with increased temperature is so altered that it dries more rapidly the longer the above treatment lasts (see Andés, "Drying Oils"). Weger found an oil so treated dried in $1\frac{1}{2}$ to 2 days, with an oxygen number of 15·1 to 16·7. Yet he found that most ozonised oils, the bulk of which came from England, contained Pb and Mn. Genthe made a series of experiments with a technically blown oil, free from lead and manganese, which he found to dry quicker than other boiled oils, which he himself had made in a manner not free from error.

Assessing Boiled Oils. The Length of Time a Boiled Oil Takes to Dry.—This naturally figures in its valuation. The maximum time has been given as 24 hours, but generally is not nearly so great. Yet the saying that a boiled oil is so much the better the quicker it dries is untrue. "Quick drying" and "good drying" are two different things. The "drying test" is used to estimate the time of drying. The boiled oil is spread uniformly either on glass or tin plate, and the gradual hardening followed up with the fingers. The estimation of the oxygen number is done in a practical manner. It is the be-all and end-all as well as a refinement of the drying test.

Method of Estimating the Percentage Increase in Weight of Boiled Linseed Oil During Drying.—The increase in weight of the oil, due to the absorption of oxygen is estimated thus: A drop of boiled oil is spread by a clean brush, or by the fingers, or a dainty spatula, in a uniform film not more than 1 mg. per sq. cm., but not too thin, on a perfectly clean and completely dry glass plate. This is then protected from dust and dirt and direct sunlight, and then left to itself at about 15° C. The film is tested from hour to hour, later on at shorter intervals with the finger-tips, until it is no longer tacky and is completely dry.

Faults of Thick Film Tests.—Thick surface drying, which occurs mostly with thick films, with a bog of undried oil underneath, fixes dust, and on drying therewith causes discoloration. Closely allied to the time of drying are the properties of the dried film. A good boiled oil should yield a lustrous, transparent solid, but elastic film (with no bog of undried oil underneath), capable of withstanding atmospheric influence.

Influence of Source of Raw Oil.—Linseed oil from Russian seed dries more free from tackiness than Indian and La Plata seed.

Superiority of Lead-boiled Oils.—In lead-boiled oils it is claimed that the oil film is more of the nature of leather, whilst manganese-boiled oil is harder and more brittle. Finally lead-boiled oil, after a certain time, shows a very strong adhesion of the oil film. Generally, blown oil does not dry very hard. A high free rosin content renders the film tacky. Rosinate of lime renders it very hard. But both are adulterants pure and simple of boiled oil.

The Personal Element in Testing Rapidity of Drying.—In testing the rapidity of drying with the fingers, the personal element intervenes so that, under quite identical circumstances, different operators may find quite different times of drying. The slightest pressure of a 6 feet 3-inch giant may go much further than the heavy pressure of a bantam. Attempts have been made to eliminate this personal element. Bandow, instead of the fingers, used small strips of paper at intervals of ½ hour. When these can be removed without part of the film remaining adherent thereto, the latter is dry.

Testing the Elasticity of a Dried Film of Boiled Oil.—To test the elasticity of the film, strips of drawing-paper were coated two or three times and well dried. Then the strips were folded twice backwards and forwards, covered with a glass plate, and the latter weighted for 24 hours with 2 kilogrammes. The folds should then show no cracks. Steensdruf hung strips of paper in the boiled oil; the quicker these dried, the higher up they rose in the filter paper. That is very questionable, as drying does not depend on body alone, but also on specific gravity. The above methods are not adopted, and the finger-nail tests have the field to themselves. For one thing the filter paper test seems inherently wrong, as every painter knows that raw oil penetrates the pores of wood very well, but boiled oil applied to wood dries mostly on the surface. Why, therefore, should filter paper be more readily penetrated by boiled oil than by raw oil?

Effect of Surroundings and Superincumbent Atmosphere on Drying of Boiled Oil.—Another defect lies in the surrounding conditions. The assertion that a boiled oil dries in so many hours, or that a boiled oil dries quicker than another, is not necessarily correct. If an oil dries in 10 hours to-day, it may take 12 hours to-morrow, and next day 8 hours. In one situation A it may take 7 hours to dry, whilst the same day in situation B it may take 9 hours. Correct figures can only be got by tests on many different days, and when the time an oil takes to dry is given, great latitude has to be allowed.

Two different boiled oils can only be correctly compared when they are both applied at the same time with one another (see Chevreul's remarks).

Normal Boiled Oil.—Weger used a standard boiled oil for comparative testing. Such a normal boiled oil is prepared in a practical way with a known weight of drier, using the newer driers, or a boiled oil must be selected, one which will not deposit any further, and which does not dry slowly.

Manganese Rosinate. Standard Boiled Oils.—As drier, manganese rosinate is chosen as the best. It is dissolved in double or quadruple its weight of pure linseed oil at 150° C. (302° F.). The solution is eventually filtered, and then diluted to an Mn content of 1·0 per cent. and of this normal solution 10 per cent. is added to raw linseed oil. But this linseed oil must itself always be of normal quality, and this condition Weger regards as still more difficult.

Lead Manganese Rosinate Boiled Oils.—In the following table is shown how the time of drying of the same boiled oil varies at different times. It also shows that the temperature at which the oil is boiled has no effect, and that with both soluble as well as with insoluble driers. All three boiled oils contained 0·18 per cent. Pb and 0·03 Mn. A was prepared in the cold with lead manganese rosinate, B with the same drier, heated for 2 hours to 260° C. (500° F.), and C with litharge, and hydrated peroxide of manganese heated for 2 hours at 220° C. (528° F.). The figures show time of drying in hours, and the three horizontal figures, the comparative results of the tests.

COMPARATIVE TESTS WITH COLD AND HOT PREPARED MANGANESE ROSINATE DRIERS AND MANGANESE PEROXIDE BOILED OILS. (WEGER.)

Samples.	A.	B.	C.
a . . .	3¾	4	4
b . . .	4¾	4¾	4¾
c . . .	5½	4½	4½
d . . .	5	7	4
e . . .	5½	4¼	4¼
f . . .	7	6¾	5¼
g . . .	7	7½	7¼
h . . .	8	7	Over 8
i . . .	7	5½	5½

Besides these rosinate-boiled oils, two oxide-boiled oils were prepared by heating linseed oil with hydrated peroxide of manganese. Drying tests gave:—

DRYING TESTS MADE ON FILMS OF LINSEED OIL BOILED WITH VARIOUS PROPORTIONS OF MANGANESE HYDROXIDE. (PER.)

	Per Cent.	Per Cent.
Per cent. of actual drier used	1·10	0·22
Corresponding per cent. of Mn	0·50	0·10
Working Mn content	0·31	0·10
	Hours.	Hours.
Time of drying, *a*	4	4½
,, ,, *b*	5	5¾
,, ,, *c*	4	5
,, ,, *d*	4	4
,, ,, *e*	4½	5½

The above results solve the second aspect of the case. With a certain Mn or Pb content the pace of the maximum drying capacity is reached. By further addition it remains constant.

Chevreul makes the following statement in regard to the drying of paint:—"There is this remarkable fact, that the resultant or sum of the activities, drying powers, of each of these substances entering into the composition of paint, cannot be reckoned by the sum of the activities of each. Thus pure linseed oil, the activity drying power of which is represented by 1985, and oil treated by manganese with an activity of 4719 will, when mixed, possess an activity of 30,828."

The following is a practical deduction from figures in following Table:—

TABLE SHOWING THE INCREASE IN WEIGHT ON DRYING OF OIL BOILED WITH 3 PER CENT. OF LEAD MANGANESE ROSINATE.

Hours.	Oxygen Absorption.
	Per Cent.
1	0·0
2	1·4
3	4·1
4	6·9
5	10·1
6	13·8
7	15·2
8	16·1
9	16·1
24	16·1

Driers not only hasten the drying process, but the metallic oxide driers formerly in so much use decreased the oxygen number of the boiled oil to a much lower figure than that of the raw oil, sometimes by as much as 100 per cent. That is not now the case with rosinate and linoleate driers. The oxygen number of normal boiled oil lies within a range of 12 to 16, others have found higher figures. Weger found 17·5, though the greater number of his figures are under.

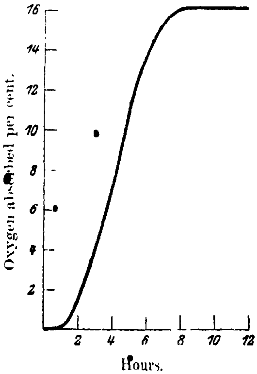

FIG. 101.

16. A typical example of the course which present-day boile undergo during the process of drying, is that afforded by a linse prepared by Weger, by treating the oil by 3 per cent. of lead ganese rosinate "in the cold".

The graph (p. 393) shows an S-shaped curve, whilst d drying volatile matter escaped. The ascending line is a straight.

The following table by Lippert seems to show that during d the film of boiled oil remains constant for a long time before crease in weight sets in. It also shows that the thickness of th may vary between 0·7 and 1·2 milligramme per sq. centimetre out the result being affected.

TABLE SHOWING STATIONARY POINT IN DRYING, AND HOW FILMS MAY BE VARIED IN THICKNESS WITHOUT AFFEC RESULTS. (LIPPERT.)

	I.	II.	III.	
Thickness of film Mg per sq. cm. . .	0·68	1·24	1·07	
Oxygen number in 16 hours. . . .	13·9	13·8	13·2	1
,, ,, 22 ,, ...	13·5	13·6	13·0	1
,, ,, 2 days	13·2	12·7	12·4	1
,, ,, 4 ,, ...	12·6	12·5	12·0	1
,, ,, 6 ,, ...	12·1	12·0	—	1
,, ,, 7 ,, ...	11·1	11·3	—	1
,, ,, 11 ,, ...	10·8	10·4	—	d
,, ,, 91 ,, ...	6·9	6·0	—	
,, ,, 104 ,, ...	6·3	5·7	—	

TEST OF COMPARATIVE RAPIDITY OF DRYING OF LINSEEI (*a*) IN SUNLIGHT AND (*b*) IN SHADE.

		In Shade.	In Sunlig
Oxygen absorption . .	1 day	1·2	1·9
,, ,, . .	2 days	4·3	13·8
,, ,, . .	3 ,,	7·3	15·4
,, ,, . .	4 ,,	11·1	15·4
,, ,, . .	6 ,,	16·6	15·4
,, ,, . .	7 ,,	16·9	15·4
,, ,, . .	8 ,,	17·1	—
,, ,, . .	13 ,,	16·4	12·4

According to Cloez, *when light is caused to pass through col glass the extent of the oxidation varies with the colour.* The mum amount of oxidation takes place with colourless glass, bu blue, red, green, or yellow, a longer time is required the near colour approaches to yellow.

Cloez was the first to point out the great acceleration exer the drying of oils by sunlight. He passed light through di coloured and colourless glass and found in the latter case that oxygen absorption occurred most quickly. Mulder confirmed the good effect of sunlight. In two of his experiments with linseed oil his film was only 3 milligramme per sq. centimetre thick, and yet his results at the present day are too low.

Mulder overlooked, above all things, the maximum absorption and regarded the process as finished in 13 days. It is readily understood that more volatile matter escaped in the sunlight than in the shade, and as Weger remarks, it is the combined action of light and heat. Day, therefore, has the advantage over night, and summer over winter. Weger found that it was best to start the drying test in the early morning. A test, at that time, gave him the result that a film in sunlight took one-half to one-third less time to dry than in the shade. According to Genthe the great effect of light is established, and, in his opinion, the special uviol light hastens drying better than any drier. The result of two tests with a boiled oil, obtained by dissolving 1 per cent. of lead oleate in linseed oil, is shown in curve A, in diffused light in B, in darkness not shown. The boiled oil took 15 days to dry in the dark, and 8 days in the light.

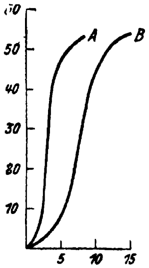

FIG. 102.

Heat exercises a very decided influence on the character of drying; oxidation takes place more rapidly, whilst at the same time, the oil being more fluid, the oxidation is more thorough, the oxygen penetrating the oil better and deeper.

Influence of Temperature on Time of Drying.—The assertion that drying is accelerated at a higher temperature is generally correct. Paint and varnish dry more rapidly in summer than in winter. Chevreul found linseed oil at 25° to 28° C. dried quicker than at 15° to 18° C. Mulder found in a test with linseed oil it took 3 days to dry with the oxygen number 0·2. The same oil in a parallel test on tin plate, heated daily to 80° C., dried in the same time, with the oxygen number 10·9. According to Livache a high temperature acts so energetically that so-called non-drying oils are converted into drying oils (!). Olive oil treated with litharge and manganese borate, and exposed to the air in a thin film, dried in 7 to 30 hours. Weger gives the following information regarding acceleration of drying at increased temperatures:—Pure linseed oil which in winter, at the normal temperature, took 5 to 7 days to dry, dried in 3 to 4 days in summer in a dark-drying oven at 50° C. in 12 hours, at 95° C. 1 hour, and at 120° C. in 30 minutes. The drying of a hydrated peroxide of manganese-boiled oil at summer temperature was 14 hours; at 95° C., 30 to 40 minutes, and at 120° C. 15 to 20 minutes. A litharge-boiled oil dries in 9 hours; at 120° C. in 20 minutes. A normal lead manganese rosinate-boiled oil dried in 10 hours; at 95° C. in 45 minutes, and at 120° C. in 15 to 20 minutes.

Effect of Atmospheric Moisture on Drying.—Mulder made no experiments, but made several remarks thereanent to the effect that atmospheric moisture must exert a great effect on the drying process. Weger did not regard this as completely proved. He placed glass slabs on which the same boiled oil was spread equally thick under two glass bell jars; one of these contained a basin with water, the other a similar basin, but in neither case did they take longer to dry—sometimes the drying was accelerated. No rule can be formulated. Lead and lead manganese-boiled oils dried more rapidly in moist air. The manganese-boiled oil, however, took longer to dry than in the capacity of a drier. Lippert tested the point, and Weger's statement was not altogether confirmed. He laid the plates at one time in the summer air, at other times in a dessicator in added air, from which, by repeated treatment with H_2SO_4 and P_2O_5, every trace of moisture was removed. The oxygen numbers found were collected in a table from which we can only give the general results. Manganese oxide, borate, and rosinate-boiled oils set quicker and dried quicker in the drying room, and the drying was accelerated the more the greater the manganese content, maximum 0·4. Generally, drying in moist air was quicker the less the Mn content. The oxygen number rises in the drying oven up to 16, the poor in Mn (content is less than 0·05) boiled oil, in moist air, gives higher numbers than manganese-boiled oils rich in manganese. With lead-boiled oil, however, the lead content of the boiled oil plays no part, and drying is affected but slightly by moist air. Only in two cases did the oil dry more rapidly than in moist air, and Lippert declares Weger's opinion incorrect. A tendency towards improved drying appears to occur with lead-boiled oil. The oxygen numbers varied from 11 to 16 and dried as well in dry as in moist air. The dry air-dried coating dried very hard, but after storing in moist air was very tacky. On taking the plates out of the dessicator a peculiar smell made itself felt—those in moist air smelled rancid. In very moist air the coats ran into one another or collected together in the form of drops.

Effect of the Drier on the Time of Drying.—Mulder on this point waged a great warfare. He gave many formulæ much too high, others far too low. Chevreul concluded that linseed oil should be boiled with 15 per cent. of metallic oxides, and Binks desired to dissolve 2 to 5 parts of lead linoleate in 1000 parts of oil. Mulder made no experiments on the point, but his boiled linseed oil with 2·6 PbO did not dry quicker when he added a further quantity of litharge or red lead. From that he concluded that 3 per cent. of drier to linseed oil was quite sufficient. To solve these questions Weger made two series of tests, using as driers a fused Mn rosinate with 2·5 soluble Mn and 50 per cent. free rosin, also a lead manganese rosinate with 8·10 soluble Pb and 35 per cent. free rosin, The driers were dissolved at 150° C. in double their weight of linseed oil, and from this concentrated extract the right addition was made to a good old-tanked raw linseed oil. A known quantity of the seccative content can be given, as the result follows the increased rosin content or the amount of deposit which occurs.

TABLE SHOWING TIME IN HOURS TAKEN BY LINSEED OIL TO DRY WHEN BOILED WITH DIFFERENT PROPORTIONS OF MANGANESE ROSINATE. (WEGER.)

Drier, per cent.	16·66	11·0	8·33	6·66	4·75	3·33	1·5
Manganese, per cent.	0·42	0·28	0·21	0·17	0·12	0·08	0·04
Hours, *a*	8·25	8·25	8·25	8·5	9	10·5	About 12
„ *b*	7	7	7	7·25	7·5	8·25	„ 10
„ *c*	7·5	7·5	7·5	7·5	7·5	8·25	10·5
„ *d*	6·25	6·25	6·5	6·75	6·75	8·5	9·5
„ *e*	9	9	9	9·5	9	9·25	9·25
„ *f*	7	6·5	7	7	7	6	7
„ *g*	6·75	8	8·5	6·75	7·5	7·5	About 8·5

TABLE SHOWING TIME IN HOURS TAKEN BY LINSEED OIL TO DRY WHEN BOILED WITH DIFFERENT PROPORTIONS OF MANGANESE LEAD ROSINATE. (WEGER.)

Drier, per cent.	6·66	4·75	3·33	2·5	1·11
Manganese, per cent.	0·54	0·39	0·27	0·18	0·09
Lead, per cent.	0·11	0·08	0·06	0·03	0·02
Hours, *a*	2·75	3	3·5	4	—
„ *b*	3	2·75	3·5	4·25	5·75
„ *c*	3·25	3·5	4·5	5·25	9
„ *d*	5	5	5·5	6·5	8
„ *e*	4·5	4·5	5·75	About 8	Over 8
„ *f*	4·75	6	7·5	„ 9	„ 10
„ *g*	5·5	7	8·5	10	„ 10
„ *h*	5·5	5·75	6	6·75	„ 10
„ *i*	4·75	6·5	9	Over 10	„ 10

When using rosinates it is useless to add to a linseed oil more than ·5 or 0·5 per cent. Pb + 0·1 per cent. Mn. The drying capacity of the oil will not be increased and a greater amount of foots will be deposited. Two further tables by Weger relating to fused manganous linoleate are not reproduced, as Weger himself does not regard the results as satisfactory. But he states that there is no use, in utilising this drier, of having a greater manganese content in the boiled oil than 0·2 per cent. He regards 0·1 per cent. as a better maximum. The following table collates results of tests made by Lippert. Their Mn content is less than half Weger's maximum. Lippert prepared his own drier by precipitating an alkaline solution of rosinate of soda by manganese acetate and dissolving the precipitate in ether. For complete evaporation of the solvent a heat of 100° C. was applied for an hour. The residue was a yellow powder containing 4 per cent. Mn. The solution in linseed oil was heated for a quarter of an hour at 150° C. (302° F.).

THE EFFECT OF ALTERING THE PERCENTAGE OF DRIER AND ITS Mn CONTENT ON THE OXYGEN ABSORPTION OF LINSEED OIL.

	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Drier	5·2	3·6	1·6	0·5
Mn	0·20	0·15	0·06	0·02
Increase in weight after 12 hours	6·5	6·6	4·9	2·1
,, ,, ,, 36 ,,	14·0	14·4	15·5	16·0
,, ,, ,, 40 ,,	14·0	14·4	15·7	16·9
,, ,, ,, 55 ,,	Decrease	Decrease	Decrease	17·0
,, ,, ,, 80 ,,	—	—	—	Decrease

From the above small content of drier it may be said the more drier used the quicker the drying, but the lower the oxygen absorption. This assertion is not confirmed by J. Petroff, who tested three manganese rosinate-boiled oils with 0·136, 0·176, and 0·220 per cent. Mn. The time of drying was 10, 12, 14½ hours. However, he used in his drying tests a thickness of film of 3 to 4 milligrammes per sq. centimetre.

Steenberg also obtained anomalous results due to the fact that he used the anomalous glass-plate method. The drying took much longer than in actual practice. As typical of his results, those obtained with a manganese-boiled oil contained 0·2 per cent. of Mn, as precipitated manganese linoleate made by himself. 0·9555 gramme boiled oil gave in 1 to 13 days the following oxygen absorptions: 2·5, 11·8, 13·7, 13·9, 14·0, 14·5, 15·1, 15·5, 16·1, 16·6, 16·7, 16·7, 16·7. These figures are shown in the accompanying graph:—

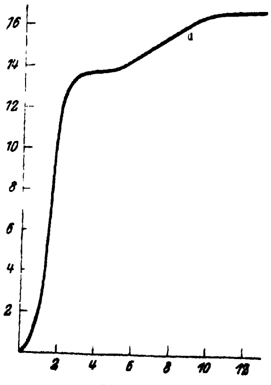

FIG. 103.

The following are additional results:—

Manganese-boiled oil, made by dissolving manganese linoleate in linseed oil at 160° C., Mn content = 0·10 to 0·95 per cent., dried quicker the less Mn it contained. 0·1 per cent. was too low, but 0·05 per cent. Mn took longer still.

Lead-boiled Oil.—Prepared similarly to above. Pb content 0·25 to 0·27 per cent., dried more quickly the more lead it contained. However, 0·27 was the maximum limit. A boiled oil with 3·50 per cent. Pb took longer to dry.

E. Tauber, as the result of practical tests, found that coats of paint in the open air, where excess of lead driers were used, were injured in hardness and durability.

A photographic plate is blackened when near to drying boiled oil (Schmidt). Paper steeped in boiled oil converts gum-arabic into an insoluble modification, as occurs with gum solutions, when exposed to sunlight for three months. The action, at a distance, of boiled oil is a sort of radiation; but neither the electroscope is affected nor the compass deviated. The permeability of bodies for radiation differs greatly; colloid bodies are very permeable. On sheet-zinc and sheet-lead oxides and peroxides are observed; with radio-activity no such things occur. However, it follows from a research by B. T. Brooks that during the drying process peroxides are produced, that the cause of the above phenomena is explained. He placed 0·1 gramme benzoic peroxide, acetyl peroxide, etc., on moist filter paper, in a crystallising dish, and covered the latter with a photographic plate. In 20 to 45 minutes a clear print was to be seen. Similarly peroxides were obtained from rosin and copal, and were made evident like the above, but not from terpenes; only the rosin acids gave an active portion.

Effect of Age on the Rapidity of Drying of Boiled Oil.—In actual practice it is firmly believed that in this respect boiled oil improves the more the longer it is tanked. Weger does not confirm this opinion. He tested the time of drying of a large series of freshly boiled oils for a period of four weeks, and repeated the same tests after a year and a half. The time occupied in drying was partly the same, partly increased, and partly decreased. Weger later made tests from the aspect that pure manganese-boiled oil, stored in open or closed tanks, remains constant in its drying capacity. Lead manganese-boiled oil remained constant under all circumstances, the slightly closed as well as the open, the slightly heated as well as the cold prepared, the oxide-boiled oil as well as the rosinate-boiled oil. Similarly, the lead manganese-boiled oil dried as well as the lead-boiled oil. Lippert later disputed this, and found, moreover, that lead-boiled oils, stored with complete exclusion of air, did not deteriorate in drying capacity.

Conversely, Weger often found that with manganese linoleate and manganese borate the time of drying extended over 8 days for complete hardening, that, moreover, such a boiled oil took over 12 hours to dry in warm weather, and a week when quite cold, in moist or wet weather; it dried well in 6 hours without separating any injurious residue.

Petroff found that a fresh manganese rosinate-boiled oil that took 10 to 16½ hours to dry, after three years took 20 to 37. But it must be remembered that Petroff used films 3 milligrammes per sq. centimetre thick.

Effect of the Nature of the Drier on the Rapidity of Drying.—Weger experimented in this direction. He asked himself the question: Will 0·10 per cent. of Mn in boiled oil, in the form of rosinate or linoleate, respectively, behave similarly? Tests with boiled oils made accordingly spoke uniformly in favour of linoleates. A further series of tests with lead manganese rosinates and linoleates gave no decided difference. Genthe found with soluble driers that the linoleate was 15 per cent. stronger than the rosinate. As the results of experiments, which the author regards as absolutely unreliable, Thomas A. Davidson asserted that rosinate driers were better than linoleate driers. Tauber got better results with manganese linoleate than with manganese borate. Lippert found that manganese-boiled oil often showed delay in setting. If alongside such a boiled oil a lead-boiled oil be applied it will dry much quicker. Steenberg confirmed the favourable working of two metals. With three rosinate-boiled oils which contained 0·25 per cent. Pb and 0·05 per cent. Mn, and 0·23 per cent. Pb + 0·05 Mn, the first dried in 13, the second in 6, and the third in 2 days.

Mulder, in virtue of his numerous researches, believed that, besides temperature and moisture, other unknown causes influence the drying. With identical weather conditions he obtained quite different oxygen absorptions, which could not all be ascribed to the moisture content of the air. He disputed the intervention of ozone in drying, and designated every unknown factor as peculiar atmospheric conditions. Weger writes in a similar strain. When one believes drying to occur with all experimental conditions equal, also that the boiled oils are uniformly spread in equally thick layers several times repeated, and at the prescribed temperature, light and moisture, yet we are in no way assured that the same result will be obtained.

Genthe found that the slightest impurity exerted an extraordinary effect on drying. He made two parallel tests with linseed oil, using the same pipette: the second experiment always took longer than the first. The explanation is that the atmospheric air was conveyed back to it each time a pipette, cleaned with chromic acid and dried, was used.

Driers: A. Detection of Solution Method.—To detect in a boiled oil the substances used as driers, Livache gives the following methods: A small quantity of the oil is poured into a test tube and shaken with dilute sulphuric acid. A white precipitate becoming black on the addition of sulphuretted hydrogen indicates lead. If no precipitation takes place, and if the sulphuric acid becomes green, blackening by the addition of sulphuretted hydrogen, the oil contains copper compounds. When sulphuric acid gives no precipitate, if the acid be neutralised by ammonia on adding ammonium sulphide, iron gives a black, manganese a flesh, and zinc a white-coloured precipitate; further, in the case of zinc, the acid solution gives a white precipitate with ammonia, soluble in excess. If, instead of using ammonia, we neutralise with carbonate of soda, iron yields a green precipitate, blackening in the air, and the original solution becomes blue on the addition of yellow prussiate of potash; manganese gives a white precipitate blackening in the air. But here Livache takes it for granted that only single elementary substances are added to linseed oil at a time, quite a gratuitous and erroneous assumption on his part.

B. Ignition Method.—The better plan, is, however, to burn the oil with the usual minute and scrupulously careful precautions observed in the ash determination of vegetable substances, and after weighing the residue on ignition to make a systematic qualitative and then a quantitative examination thereof. Zinc oxides and salts are, however, liable to become reduced and then volatilise and escape recognition. The methods given in books for the determination of mineral substances in oils are quite unreliable, and none more so than those of Benedikt. A *systematic* examination of the ash is the only reliable method. Each individual mineral element present in the oil must be separated out and quantitatively determined. It is most unscientific to estimate lime in the analysis of the ash of oil in the same way as is done in the case of marble; we know beforehand that the marble is almost chemically pure carbonate of lime. As to the ash of an oil we know nothing whatever, and to proceed to its analysis with preconceived notions by groping in the dark shows very bad training on the part of the analyst, whoever he may be.

CHAPTER XV.

DURABILITY OF PAINT.

Linoxin.—The skin left on the drying of boiled linseed oil cannot be described as linoxin without great latitude. It contains (1) a known weight of metal, and (2) with rosinate boiled oils a known weight of rosin. The rôle of the metal content is to render the coating harder, and thus resist the abrasive action of reagents, sand, and the weather; elsewhere it has been pointed out how raw oil is added to boiled oil to render the coating more elastic. Rosin behaves so that a certain percentage has an injurious effect, and the disintegration of the paint later is accelerated. The boiled oil is nearly always mixed with inorganic pigments. Some of these are quite inert, e.g. barium sulphate; some, however, are basic and act on the boiled oil, which, if only present in small quantity, is saponified; amongst these white lead as demonstrated by Mulder. That boiled oil probably reacts during drying with zinc sulphide, an ingredient of lithopone—a white paint which also contains barium sulphate—has been shown recently by Meister. Paints frequently contain turps, which has either been used in the liquid driers or as a thinner. Paints also contain a deal of thickening ingredients, paraffin wax, Japan wax; above all things they are ground in stand oil. Mactear proposed to use strontium hydrate and barium hydrate as alkaline earth thickeners. The desired properties in a coat of paint are a certain amount of elasticity and a certain coherence, inert to gases and fluids. Owing to the variations in temperature it is apparent that the coated surface must necessarily undergo contraction and expansion. Now the coefficient of expansion of the under coat, the pigments and the linoxin, are quite different, and the difference must be equalised by the elasticity of the linoxin. Finally, the pigments as used to make paint are in the form of a fine powder; the linoxin must not only bring the necessary coherence but must be of such proportional composition as to adequately provide an efficient protective expansive coating or layer throughout the whole.

These properties, Mulder claimed, were fulfilled by linoxin. Linoxin was born when it received the impulse given to it by the Dutch painters Hubert and Johan Van Eyck, who are so erroneously credited with being the first to use linseed oil in painting. Water-colours dried duller in tone; finally they dried so quickly that the layers did not flow together; if it was desired to form a certain design there was a lack of harmony in that design. Finally water-colours gave a non-transparent opaque film, and upper correcting coats were impossible. However, that was all changed when boiled oil appeared on the scene as a new ideal vehicle for painters' colours. It has a certain consistency which the solid oil colours do not increase. It spreads well and dries so gently that further coats of paint can be applied, but not all present-day experiments must therefore be regarded *cum grano salo.* Moreover, the nature of the pigment exerts an influence on the permeability of paint. Paints containing lamp-black and ochre, are, it is asserted, generally permeable. Red-lead paints and white-lead paints are said to be less so, and zinc oxide still less. But such opinions conflict too much with others. Ordinary lamp-black abounds in greasy tarry oils, and any test made therewith without calcination is invalid. Ordinary ochre paint grates under the palette from the presence of hard particles of grit, and sharp hard particles of barytes (some paints look as if the makers had been trying to make a composition for razor strops or emery paper). White sharp, hard particles should not shine out of paint like particles of mica from a micacious sandstone. Remove the tar, etc., from lamp-black by calcination. Put the yellow ochre through the 200 to 300 mesh sieve, now being used in the U.S.A., and try the permeability of the paint once more. But as Treumann had to acknowledge, there is no reliable test for permeability, as the same paint gives different results when several tests are made simultaneously. But the best test is the impermeable waterproof garments, in which oxide boiled linseed oil is the sole ingredient, and the impermeable airproof and waterproof herring-net buoys. The makers of these have to give linseed oil a fair field. They only deviate from linseed oil to their cost and their sorrow. If thoroughly dried linseed oil were as pervious as clumsy experimenters with no experience of the oil-waterproof garment industry, and who ignore the waterproof nature of real good genuine putty, would have us believe, then the linseed oil-waterproof garment industry would have been still-born or stifled at birth.

Microscopic Faults of Paint Films.—It has been pointed out that when a working painter gives several coats of paint to a glass plate, faults can still be seen under the microscope, and when a coat appears quite thick it becomes thin in the course of time, and then under the influence of variations of temperature and unequal expansion, microscopic hair cracks are to be seen.

The Supposed Permeability of Paint Films to Water.—C. P. Dudley concluded that the dried oil-skin was permeable to water. He dissolved 30 grammes of dextrin in a mixture of 40 c.c. water and 50 c.c. alcohol, and spotted some of the above solution over several cm. of a glass plate, dried it at 65° C., and then coated the plate repeatedly with boiled oil, then the plate was placed in water for 12 hours. The dextrin was uniformly flaky, a proof to the author that the water had got at it. But Dudley begs the question that boiled linseed oil dries satisfactorily on a coat of dextrin. When pigments were mixed with the oil, the permeability decreased (Quite so; the contact of the oil with the unstable dextrin was diminished); not so quickly that the new coat combined with the old one. Completely dry films can be wet with oil and new films formed. The paint coat is so elastic that the expansion and contraction of the undercoat follow as a necessary sequence. The films of paint are transparent, so that any single pigment in all its beauty and apparent harmony can come into play. Oil paints bring a new vivacity, and Mulder regarded linoxin as completely unattackable. He prepared paints so that boiled linseed oil (made with 2 to 3 per cent. PbO) was mixed with 5 per cent. of finely pulverised red-lead, and with 40 to 200 of an indifferent powder, sand, pipe clay, clay, ironstone, ground pumice, etc. First he coated an iron plate on one side, and exposed it for a month to wind, water, rain, and sunshine. The uncoated side was covered with a thick layer of rust. On the coated side the coat adhered firmly and little rust could be observed. Mulder's claims as regards linoxin are not accepted by interested parties as demonstrated, and to-day other opinions are to some extent held. Treumann does not regard oil-skin as impervious, and holds Mulder responsible for the belief that it is impervious. During the drying of the under-surface of the coat of paint, it is softened by the vapour of water and carbonic acid, so that the coat of paint must be permeable to both carbonic acid and water. It is evident that the volatile products generated in the first stage of drying escape as gas, and the resulting pores are widened in the second stage. If these pores be only small they go down right through the paint to the surface of the object on which the paint rests underneath.

Treumann spread boiled oil and paints on glass, metal, or porcelain and left them to dry, then he placed the plates under water at the ordinary temperature. Sooner or later cracks or blisters were formed. The skin did not decay, but its adherence to the surface underneath was partially broken up. But in actual practice, except with anti-fouling compositions, paint is not generally exposed under water. Therefore, in Treumann's researches conditions are brought into play which do not prevail in actual practice. A pair of boots kept in a tank of water for a year would then be a very sorry pair of boots indeed. But does that detract from the value of leather in many of the 1001 uses to which it is put? No! Neither does the damage done to a dried linseed oil film by soaking it in water detract from its general use. It is curious that no attempt has been apparently made to test the behaviour towards water of a baked film of linseed oil, and it is forgotten that good putty is impervious, as hundreds of millions of windows testify. Nearly all experiments in which linseed oil turns out badly would, if traced to their source, be found to be dictated by those who want to market a linseed oil substitute, or some pet composition, and who wish to prove that linseed oil has all the defects of their own products and none of their good qualities.

It is asserted that when the least quantity of red lead is mixed with the least possible quantity of linseed oil, a completely water-tight coating results. When the latter forms no protection against rust that must be attributable to other causes. W. Thomson believes that during the inter-working between the iron and the metal in the boiled oil a slight galvanic current ensues. E. Fauber also thinks that weak galvanic currents are the key to the formation of cracks in paint. The permeability of paint to water is attributed to the hygroscopic nature of linoxin. Treumann placed a completely oxidised air-dried and clean oil film on a watch glass, and the latter with a vessel partly filled with water under a bell jar. The increase in weight of the films in 4 to 8 days was 7 to 15 per cent. and the water absorbed was ceded on exposure to the air. These figures are very high, Mulder's and Weger's were much less. When Mulder heated dried linseed oil, or dried boiled oil to 80° C. (194° F.), the linoxin lost 4 per cent. in weight. The plate left again in the air only gained 1·2 per cent. Mulder believed that the linoxin contained the condensed vapour.

Linoxin.—Weger placed well-dried oil-skins in a dessicator containing neither water nor H_2SO_4. He found a difference up to 2·4 per cent., but such differences in the moisture in the air do not occur in actual practice, and the effect of the moisture variation lies under ½ per cent. Doubtless, therefore, the assertion of W. Jones that a boiled oil dry film absorbs water like a sponge is incorrect.

The very excellent qualities of linoxin are not everlasting. Like all organic substances it goes under later on. Light soon acts on it. Mulder found a brown coloration of the inner half within a month. Under the action of direct sunlight the brown coloration is changed and the coloured portion of the oil affected. Above all it is the oxygen of the air which first dries the oil but does not, however, leave the dried film unaltered.

Action of Sunlight on Oil-paint Films.—Toch found that paint altered much under the action of light. White pigments turn yellow under the action of the Pb and Mn present in the boiled oil, the zanthophyll of the linseed oil is reduced to chlorophyll. In bright sunlight white colours are formed. According to Lippert a boiled oil dried in darkness becomes red-brown, in direct light the bleaching is further accentuated.

Now let us point out the number of tests which should be made. For the sake of argument, let it be accepted that only thirty pigments have passed the dry test, and every one of these thirty colours is to be ground in the five oils aforesaid, in three different proportions of oil and pigment, the mixed colours put on glass plates, and for each there must be five plates for the different experiments. The mixing of the oils with other mediums could be very different, quantitative as well as qualitative, and there would be no limit to the number of tests; therefore, we will limit ourselves to five different liquids, and we find that we have four thousand five hundred tests.

This does not exhaust the subject by any means, because the colours could be mixed two or three together, and also tested; but I shall not undertake to recount the possible number, because it might strike terror into the hearts of my readers, and they would doubt the possibility of such an undertaking. Although the solution of the problem in the foregoing is very complicated and time-robbing, it could be solved nevertheless if a special laboratory were provided for the purpose.

The prepared pigment colours would be compared, and then weighed. Comparison by observation would have to be made often in the beginning, to note the time of changes in each sample and the apparent cause thereof. Only after several years, however, would it be possible to form definite conclusions and adopt rules governing the use of oil colours. This would be a costly experiment, but one that appears promising.

More simple, perhaps, would be a direct use of the samples prepared. Apparently it would be enough to make about thirty painted panels and expose them. In a few years they could be compared, but this would be a waste of time, because it would be impossible to tell which part of the oil colour has had the most influence in changing the tone of the same.

1. The permanency under exposure to light of pigments in powdered form is in many cases perfectly satisfactory; in others it depends on the mode of preparation. Several grades of quicksilver vermilion are entirely unfit for the use of the decorator, because they assume a brownish tone very soon after exposure to sunlight. The so-called mountain cinnabar is the only durable pigment of that character. A few samples of cadmium yellow, deep and orange, from reliable firms, turned after a time from their original tone to that of pale ochre.

2. The colours described in the foregoing paragraph, when ground in oil, resisted the action of light slightly longer, but the result was comparatively the same. In these pigments, when ground in oil, there are certain optical changes, brought about by the action of the pigment and oil upon one another. When balsams or resins are added to these oil colours, the changes are delayed much longer, because the colours are protected from the action of light and air more effectually.[1]

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[1] *Example.*—Cadmium yellow containing a sulphur content is an unsatisfactory pigment by reason of the fact that it cedes sulphur to oil owing to such sulphur being, so to speak, loosely combined in the cadmium salt. Presence of sulphur in a simple linseed oil film (linoxin) causes its speedy disintegration. The addition of select balsams and resins to such oil mixture (paint) will lengthen the period for disintegration.—C. Harrison.

3. The contraction of one and the same colour, ground in different oils, proved of different character; also the contraction of different colours in the same oil. The larger the quantity of oil used the greater is the contraction in drying, but it must not be concluded that colours which require more oil than others also show a greater contraction. The great decrease in weight and in volume, which is very much varied in the different colours, points to a greater or lesser energy in the chemical processes which occur in the colours. So, for instance, the volume of barytes ground in poppy-seed oil in two years decreases less than 3 per cent., while that of pure white lead, ground in poppy-seed oil, decreases 18 per cent. in the same time, showing the great chemical action and affinity between white lead and oil.

4. The optical character of the colours is also dependent on the oil; each of the five oils enumerated is best adapted for certain pigments, but a conclusive rule on this point needs the expenditure of much time and the making of manifold experiments.

5. The colours of the future should have their exact composition on the label; such colours could be used in painting as well as for experimental trials. The colours as bought contain variable quantities of oil and other admixtures, and are not useful or safe for forming conclusions.

6. Siccatives or driers hasten the chemical process in colours, but decrease the durability; the use of these is often necessary, but they should be employed with skill.

7. In painting on canvas it is of great benefit to give the thin roundwork a good drying in sunlight, but a finished painting should ot be exposed; the chemical processes should be retarded by adding alsams or solutions of resins, and the back of the canvas coated with good varnish.

8. The addition of resins and volatile oils is, on the whole, admisible and well founded, but it should be determined by previous tests hat the colour does not become brittle by such addition, and that, on ccount of the rapid evaporation of the ethereal oils, the cohesion of he particles of colour is not decreased.

9. The number of colours used in painting should not be too imited, because in such case the demand of the present time could ot be satisfied. But the number should not be unnecessarily inreased, because in such a case there would be too many new and nknown chemical properties whose characters would not be undertood. The opinion that it is possible to get along with seven colours, ecause all the colours of nature are composed of seven tones, is rroneous. The blending of the natural strata and the creation of he tones by mixing of material particles follow different laws.

Decay of Paint.—The natural oils capable of drying to a solid lastic insoluble film do not do so at all rapidly and occupy several ays in drying, during which the paint still remains tacky and records he impression of the finger or thumb however lightly applied. Moreover, the soft paint is during all this time fixing all the passing dust on to its surface. As a matter of fact, painting in oils was impossible until certain substances were discovered, which when added to the drying oil increase the drying of the paint. In distemper painting (with glue albumen and casein and the like) the coat of paint only dries after all the water is evaporated.

In inside coatings, white paint nearly always turns yellow, which in some cases is remedied by a little ultramarine, but such quick process patent white-lead paints as contain lead peroxide are altogether too dirty in shade to be toned down by any addition.

Action of Internal Organic Peroxides on Oil-paint Films.—Fahrion believes that when linoxin is present in a hidden form it still contains active oxygen, and that it is from that active oxygen that the decay proceeds. The peroxide group acts spontaneously when, not long after it is fixed by the ketoxy group, the hydroxyl group so formed splits off water, diminishing the volume and thus forming cracks. This hastens the ultimate decay of the coat, and, it is claimed, leads, as Reid has shown, to the formation of water-soluble bodies by further oxidation. But of all that we have not one particle of positive proof, and much which flatly contradicts it in every way it is possible to conceive.

Pettenkorfer's Method of Restoring Old Oil Paintings.—A short notice may be given here of Pettenkorfer's method of restoring old paintings—oil paintings that have become stained. It consists in exposing them for a longer or shorter time to the vapour of alcohol.

Effect of Pigments on Linseed Oil.—The constants, including yield of ash, of raw linseed oil mixed with white lead in paste form showed no material change in 25 months. Storage in partially filled containers for a year of raw linseed oil mixed with white lead and with white zinc in the proportions of paint ready for use, and exposure to air of films of such mixtures, resulted in sufficient combination of oil and pigment to cause the extracted oils to yield amounts of ash that were much larger than those obtained from the oils used to prepare the mixtures. Exposure to air of films of these pigments mixed with boiled linseed oil also caused appreciable combination of oil and pigment. When white lead and white zinc were mixed with linseed oil fatty acids considerable combination of pigment and fatty acids occurred. The amount of fatty anhydride combined as zinc soap was nearly four times as great as that combined as lead soap, the calculations being based on the amounts of ash yielded by the ether extracts of the pigment—fatty acid mixtures and the ratios of the combined weights of zinc oxide and lead monoxide. The results as a whole indicate that white zinc combines with the free fatty acids of linseed oil more readily than does white lead. Of the three pigments, white lead, white zinc, and china clay, the former showed the greatest accelerative effect on the oxidation of raw linseed oil in films composed of pigment and oil, while china clay had the least accelerative effect.

When a mixture of raw linseed oil and china clay was kept in a partially filled container for one year, the constants of the oil were materially changed, while raw linseed oil with chrome yellow and with zinc yellow under the same conditions showed practically no change. In drying films, however, the accelerative effects of the two yellow pigments on the oxidation to the oil were much greater than that of china clay.—U.S. Bureau of Standards Technologic Paper No. 71.

The permanency of pigments ground in varnish is discussed in Vol. III, pp. 437-9, also the reaction of solutions of resins on colouring principles especially from coal-tar.

Here we look at another aspect of the question.

Testing the Permanency of Dry Pigments Under the Action of Light and the Durability of the Paint Formed by such Pigments as have Stood the Test.—Pigments ground in oil are known as oil paints or simply paint. They are thinned with hydrocarbon oils, e.g. turps, or other volatile solvents, e.g. white spirit or turpentine substitute, so that they can be spread out into a more or less thin film with a brush. But the paint must not be thinned down so far for its binding vehicle to be attenuated too far. This film, soft at first, gradually hardens, and in the course of time loses, as it ages, its original toughness and elasticity. Then is the time when cracks begin to appear on fixed painted surfaces, but on a painting on canvas rolled up for convenient handling when moved from one spot to another, cracks appear on the painted canvas a few months after the painting is finished. The tint or tone of oil pigments or paints changes rapidly. Changes in like pigments due to bad washing must not be ascribed to the pigment itself. The trained eye accustomed to assess variations in tint will readily notice such a change in a few weeks, and within a year the change is very readily perceptible, however well prepared and permanent the pigments used may be *per se*. As a whole, colours ground in oil are not permanent, and the painter must rest satisfied if after a reasonable lapse of time the change in tone has been only a slight one.

Paint Changes and Hardens from Two Different Causes: (1) *The Oxidising Action of the Atmosphere and* (2) *The Mutual Action of the Pigment and Oil.*—The first and chief cause is well known, the second cause is undoubted. Some pigments retard drying of oil, others hasten it. But as the hardening of each of the various paints differs in itself, the cause of the difference must be sought for in the chemical action between pigment and oil. The weighing of glass slabs, covered with films of different paints, has proved that in such paints there are changes in weight on drying and to very different extents.

Testing the specific gravity and specific volume of these glass slabs by weighing the slabs in air and under water there is a loss in volume although varying widely with different paints. These tests show that in drying out the film of paint loses its original elasticity, which loss is increased as the volume decreases, and therefore there must be a tearing apart which ultimately shows itself in cracks. It must not be supposed that the percentage of loss is very large, and it requires the most sensitive scales and years of labour to find a loss of one-fifth of 1 per cent. in some paints, whilst in others the loss was as high.

It may take 20 years' observation to find the exact time when the hardening process in a paint ceases. Molecular changes are also possible which do not alter the volume but influence the elasticity and so bring about scaling or cracking and "chalking". The mutual action of pigment and oil is most perceptible in the oil, yet the pigment also changes, and although it may not alter its chemical character yet the colour tone varies from the original.

The tone of colour is subject to alteration whenever a molecular change can take place; such changes of tone are most feared by painters. All coloured paints in their physical and chemical nature are materials which in time destroy themselves, and the only method to obtain the longest possible durability is to arrest this physical chemical process by suitable additions in thinning. Such apparent defects in paints might induce the painter to seek a remedy in other vehicles or media. All experiments in that direction deserve the special appreciation of artists. But oil paints possess such merits and optical properties that of necessity painters are as yet and will be for some time to come compelled to use oil, linseed oil more especially, and to add other materials to assist in drying (driers) and in spreading thinness. While oil cannot be done without as a medium and binder it is necessary to look for other materials to assist in giving oils greater stability. The changes which take place in paints are a special case of very complicated phenomena, whose explanation lies in the thorough study of the composition of oils and pigments and their mutual action on each other. But oil, let it be well understood, is not a body of definite chemical composition, and here is the stumbling-block in experimenting with paints and oil painting. There is another remedy, namely, to critically examine the materials which have so often proved themselves to be good. To make error impossible there should be a uniform method adopted for these tests. The colour most adapted for the purposes of the painter should be obtained in the dry state in powdered form and exposed in thin layers to moist strong light in dry and moist atmosphere, and the results closely observed and registered. To hasten the trials the powdered pigments should be exposed to sunlight and to such gases as are present in rooms. Those pigments which have shown themselves light-proof and resistent to gases should be separated from the others, ground up in oil, and then tested in the same way, and also painted out to find whether after drying cracks are perceptible with the aid of a magnifying glass. The paints so obtained should also be tested by adding boiled oil, solutions of resins, balsams, essential oils, etc., and observations made as to elasticity. In oil painting three drying oils are principally recognised:—

1. Linseed oil.
2. Walnut oil.
3. Poppy-seed oil.

But two more should be tested:—

4. Sunflower-seed oil.
5. Hemp-seed oil.

The first, sunflower, has the property of excellent transparency. The latter, hemp-seed, is valued in Russia on account of its highly developed resisting power to sunlight and atmospheric influences. Commercial hemp-seed has a greenish colour, but when expressed cold it is very light, and if filtered through charcoal is then colourless.

CHAPTER XVI.

DRYING OILS OTHER THAN LINSEED OIL.

1. *Acacia Oil* (*White*).—This oil is described, in its proper place, as Robinia or Locust-tree oil, a gigantic tree. It is not derived from an acacia.[1]

Argemone Oil, from *Argemone mexicana*, of a yellow colour, inclined to orange, is specifically lighter than poppy-seed oil. It does not dry so well as the latter. Its diminished density would appear to be due to the fact that it contains volatile fatty acids, acetic, butyric, and valeric, but Crossley and Le Seur failed to identify these in two genuine samples. This little-used oil is purgative in doses of 15 to 30 drops. Its taste is biting and its smell nauseous. These samples had the respective acid numbers of 6·0 and 83·9. The last sample therefore was completely soluble in absolute alcohol at 60° F. The seeds of Argemone mexicana, called *fico del inferno* by the Spaniards, are said to be narcotic, especially if smoked with tobacco, and purgative. They are used in the West Indies as a substitute for ipecâcuanha, and the juice is considered by the native doctors of India as a valuable remedy in ophthalmia, dropped into the eye and over the tarsus, also as a good application in cancers. It is purgative and diobstruent. The Brazilians administer the juice of this plant to persons or animals bitten by snakes, but, it would appear, without much success.

Castor Oil.—This oil has been so frequently described in the different treatises issued by the publishers of this volume that the author refrains from adding another description to the number, the more so as it has nothing in common with drying oils, and the wider the berth the paint-grinder and varnish-maker gives it the better. The oil is adequately described in Hurst's "Soaps," Hurst's "Lubricating Oils," "Textile Soaps and Oils," Andés' "Vegetable Oils," Andés' "Drying Oils, Boiled Oil, and Solid and Liquid Driers". The action of nitrous acid and nitric acid are somewhat interesting and thus deserving of mention, the more so as they are included in the stereotyped descriptions of castor oil.

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[1] *Acacia Oil* (*Yellow*).—This oil is not described here as it has no *locus standi* neither as an acacia oil or a drying oil; it is only a semi-drying oil, and is only mentioned here to point out that neither is it derived from any acacia; moreover, further than that the two plants Robina and Caragna belong to the Legumenosæ they have nothing else in common. The so-called yellow acacia is derived from a shrub whose specific name is Caragna..

Action of Nitrous Acid on Castor Oil.—Boudet termed this palmine, but it is more generally known as recinelaidin. When nitrous acid (or nitrite of mercury, as stated under the head *olive oil*) is made to act upon castor oil, it is converted into a solid wax-like substance; but this change is much less rapid than that which ensues when olive oil is similarly treated; and it deserves notice that castor oil is the only one of the *non-drying oils* which is susceptible of this species of solidification.

On adding nitrous acid to castor oil a yellow liquid is at first formed, and the time required for its solidification varies with the quantity of acid employed; when about $\frac{1}{20}$ part of acid is used, it solidifies in 7 or 8 hours, and this, or somewhat less, is the best proportion. If too much acid be used, a third part, for instance, or a half, the temperature rises to 130° or 140° F., effervescence ensues, and the oil becomes opaque, and instead of indurating, remains viscid.

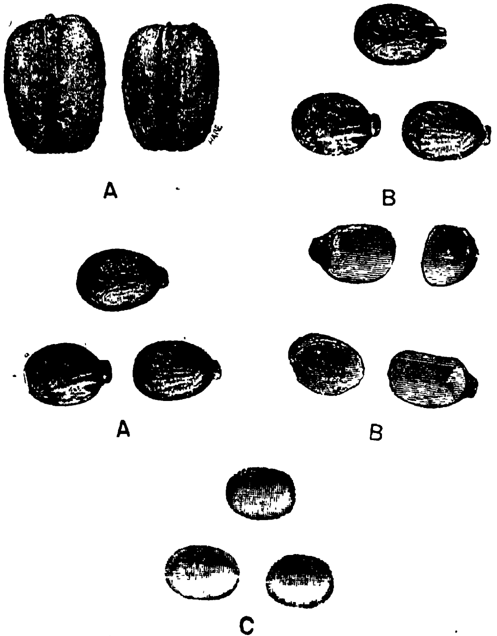

FIG. 104.—Castor-seeds.

Recinelaidin thus obtained is yellow, but when purified by solution in boiling alcohol, it is white, of a waxy fracture, and requires a temperature of about 150° F. for its fusion. When kept for some months, it occasionally acquires a resinous appearance, and presents an almost vitreous fracture. It has a peculiar odour, appearing to arise from the presence of a volatile oil, and when distilled with water, the distillate has an aromatic odour, but no trace of an essential oil passes over. At the temperature of 96° F. alcohol dissolves about half its weight of recinelaidin or palmine; it is much more soluble in boiling alcohol, which, on cooling, deposits it in small opaline, but not crystalline grains. It is very soluble in ether: indeed, when in fusion, ether dissolves it in all proportions.

When recinelaidin is heated in a glass retort, it appears to boil, disengages gases and aqueous vapour, and a peculiar volatile oil passes over, after which the residue suddenly swells up into the neck of the retort, forming a porous resinoid matter resembling that produced during the distillation of castor oil. The volatile oil amounts to about half the weight of the palmine, and when redistilled with water, yields about a third part of an odorous volatile oil, and leaves a more fixed oil which is very acid, soluble in alcohol and in weak solution of potassa, and remains fluid at 32° F. When this acid oil is triturated with a tenth of its weight of calcined magnesia, the mixture heats and thickens, and ultimately forms a brittle transparent compound, easily soluble in alcohol.

When recinelaidin is boiled in a concentrated solution of potassa, it exhales the characteristic odour of its peculiar volatile oil, and is easily saponified, though less rapidly than castor oil; glycerine is separated and a saponaceous compound formed, soluble in alcohol and in water. This soap is entirely separable from its aqueous solution by the addition of common salt. When its solution is decomposed at a boiling heat by hydrochloric acid, a peculiar fatty acid separates, which concretes into a crystalline mass on cooling: this is recinelaidic acid.

Recinelaidic acid forms stellated groups of acicular crystals, fusible at about 120° F. and very soluble in alcohol and in ether; it reddens litmus, and expels carbonic acid from the carbonates. When heated a part of it volatilises without decomposition; a portion of empyreumatic oil is also formed, and carbon remains. The greater number of the recinelaidates are soluble in alcohol; recinelaidate of silver is insoluble in water.

Cedar-nut Oil. Siberian Pine Oil.—This oil is derived from the *Pinus Cembra*[1] (*Pinus Siberica*). The proper name of this oil should therefore be Siberian Pine Oil. The pine tree which yields it has little or no claim to being classed as a cedar, and it is classified by Kew as a European pine. The seed of the cone, the so-called fruit, yields an oil which is said to be manufactured on a larg scale in Siberia. The tree is common on the Swiss Alps where it i usually met with at altitudes of 5000 to 7000 feet, and in variou parts of Switzerland it is grown up to 8000 feet for protection purposes, where cold and exposure are too severe for Scots pine. I both Siberia and Switzerland the seeds are used for food.

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[1] A writer in the "Kew Bulletin" tells us that although *P. Cembra* was introduced to the British Isles in 1746 really fine examples are uncommon, very few specimens being on record which have attained a height of 70 feet or more. In E. Russia and Siberia it grows 120 to 130 feet high with a clear trunk of 60 to 80 feet. But in Scotland the nurserymen of that country flatly contradict Kew and strongly recommend the tree.

TABLE SHOWING THE CHEMICAL AND PHYSICAL CONSTANTS O CEDAR-NUT OIL.

Density at 0° F.	0·930	L. V. Schmorlling.		
Solidification-point	– 20° C.	Krylos.		
Acid number	1·09	Schmorlling	3·25	Krylos.
Reichert ,,	2·0	,,	3·77	,,
Iodine ,,	159·2	,,	149·5	,,
Hehner ,,	91·97	,,	93·3	,,
Saponification number	191·8	,,	191·8	,,
Increase of temperate with H_2SO_4 (Maumené)	98° C.			

FREE FATTY ACIDS.

Mean molecular weight	280 to 290 (*a*)
Solidification-point	11·3
Acid number	193·1
Acetyl ,,	81·9 in 6 days.
Iodine ,,	161·3
Iodine ,, of the fluid fatty acids	184·0
Fluid fatty acids (Mulder)	87·0
Unsaponifiable	1·3
Glycerine	10·1

Candle-nut oil is derived from a species of *Euphorbia* which rejoices in three scientific synonyms :—

1. *Aleurites triloba*, Hemsley ("Kew Bulletin," 1906, No. 4, p. 121).
2. *Aleurites Moluccana*, Wild, to which has to be added,
3. *Aleurites ambinux.*

In familiar language it is spoken of as—

(*a*) The Indian or Belgaum walnut tree.

(*b*) Candle-nut tree.

In the French language it is known as Le Baucoulier.

In native Indian language the tree is termed the Jangli akerot; Jaiphal, etc.

Synonyms of the oil :—

English—Candle-nut oil.
Kekune oil.
French—Huile de noix de Bankoul.
German—1. Lumbang Öl.
,, 2. Kukui ,,
,, 3. Bankul ,,
,, 4. Litnuss ,,
,, 5. Lackbaum ,,

Further than that this tree belongs to the *Euphorbiaceæ* or *Spurge worts*, the special literature gives little information as to its habits and mode of growth. It appears as if it only attains a medium height in the Moluccas, the country of its origin; in New Caledonia it seems to thrive much better, attaining as a matter of fact a considerable development, reaching a height of 60 feet by a circumference at the base of 5 feet. Its growth is rapid, and it begins to bear fruit at the end of four years. The fruit is a fleshy drupe, generally formed from a single incompletely developed cell. The seed is enclosed in a hard shell, encrusted with a calcareous efflorescence when it falls to earth. It burns very regularly and gives off great heat and a very thick black smoke. The kernels are sometimes strung on thin bamboos and burned as natural candles, hence the name "candle-nut tree". The nut weighs about 10 grammes. The oil extracted from its kernels usually weighs between 6 and 7 grammes, and a tree may bear about 2000 nuts or 20,000 grammes, and as 1000 grammes equals 1 kilogramme, we get 20 kilogrammes or 44 lb. of nuts as the produce of one tree.

Extraction of Candle-nut Oil.—Field-Captain Champion describes the preparation of candle-nut oil in Ceylon. He says it was in 1843 exported from Ceylon as kekmedic. The nuts are said to contain 50 per cent. or more of a sweet edible oil (Dymock, "Mat. Med. West India," 617). It is highly valued as an illuminant and said to be largely exported from Polynesia, and used in the candle trade of Europe. The most primitive process consists in exposing the nuts to the sun for some hours. The kernel loses its water, then becomes easily detached from the shell in a single mass, and at the first stroke of the hammer. The ground kernels are placed in small heaps on an inclined metallic plate, the whole is exposed to the sun, the oil exudes slowly, losing any water which it may still retain, and flows through the grooves of the plate into a collecting vessel. It is then filtered. The yield by this semi-barbarous process is poor, barely exceeding 6 per cent. By cold pressure the amount may be raised to 29 per cent., and by hot pressure it may reach 34 per cent. If the oilcakes be again treated the yield may be 66 per cent. The explanatory figures state that—

100 kilos of nuts produce on an average 33 kilos of kernels.
100 kilos of kernels produce 66 kilos of oil.
100 kilos of nuts then give 22 kilos of oil.
1000 kilos of nuts, or 1 ton, costs in Tahiti
£6 and for freight
£3 4s.
£9 4s. in all.

But it is stated, on the other hand, that the kernels are sold at £16 per ton, and 1000 kilos of kernels, or 1 ton, yield 660 kilos of oil or 13 cwt., and if 13 cwt. of oil costs £16, 1 ton of oil will cost £24, or 24s. a cwt., excluding the cost of crushing.

The candle-nut tree nowhere occurs plentifully, except in Malasia, even if it be practically distributed throughout all India and Burma. It is said to be wild in the Wynaad as it is abundant there, but it is not a native of India, and generally grows as a roadside or garden curiosity near towns or villages. In Eastern India the fruits ripen from June to August (Roxb., Kurz), but in Western India not until the cold season (Talbot). During the succeeding half-century the Indian press as a whole have from time to time urged the importance of cultivating this tree, but with little or no effect. If, as already mentioned, the tree exists here and there all over India, it nowhere occurs in such abundance, it is pleaded, as to hope for any immediate commerce in the oil. The oil does not appear to be expressed anywhere in India, except in the Shan States. In some parts of Burma it is used as a varnish for lacquer ware, but according to Sir George Watt, it is usually stated that for that purpose it shows no advantage over sesame or sarson (rape oil).

Properties of Candle-nut Oil.—The oil when crushed in the cold is of a pale yellow with a pleasant odour, whilst hot crushed oil is brown with a bad smell. It dries somewhat about the same time as linseed oil. Like linseed oil its drying properties can be improved by "boiling" with driers. It then yields a boiled oil with very appreciable drying properties. Various Paris firms have in this way obtained excellent results. Andés tested candle-nut oil as to its suitability for boiled oil and varnish-making. Small quantities of the crude brown oil were boiled with litharge, red lead, lead acetate, and manganese borate respectively. The lead-boiled oils were all very dark in colour. At 140° C. (284° F.) the oil gave off bubbles. It was kept at that heat only for a short time, the reason being, as explained by Andés, that he was working on a very small amount of oil. The boiled oil smelled like the raw oil, only somewhat more unpleasant. The manganese borate boiled oil did not alter in colour. The boiled candle-nut oils were said by Andés to dry 4 hours sooner than well-boiled linseed oil! The boiled candle-nut oils dried at least 4 hours before the boiled linseed oil, even the raw oil itself also dried more quickly than raw linseed oil. At 325° C. (617° F.) candle-nut oil gave off vapours with a very strong unpleasant smell. After the oil had undergone partial destructive distillation and a loss of 20 per cent. by decomposition occurred, there resulted a thick soft mass as in the more partial destructive distillation of linseed oil in Mulder's milder experiment. But the colour according to Andés was almost black, due to the presence of much admixed impurity. In any case, no drying oil can be heated to 617° F., without showing change of colour. Similar experiments were performed with the white oil. Nearly all the oils boiled with lead were dark in colour, whilst the manganese-borate-boiled oil was only slightly yellow. In the drying tests the pale candle-nut oil showed the same advantage over linseed oil as the brown oil, and dried some hours sooner. But when pale candle-nut oil was heated to 325° C. (635° F.) it was found that after 20 per cent. had undergone partial destructive distillation, the oil bleached to a colourless white syrup. Andés reports that the durability of earth-coloured paints or metallic oxide paints with candle-nut oil as a vehicle, gave the same results as were obtained with boiled linseed oil. But owing to the scarcity of candle-nut oil on the market there is little hope of its use becoming general.

De Negri examined candle-nut oil from seeds of *Aleurites triloba* (Hemsley) and of *A. Moluccana*, Wild. By extraction with solvents he obtained 62 per cent. of oil, but it did not dry as well as Chinese wood oil from *Aleurites Fordii.*

TABLE SHOWING THE CONSTANTS OF CANDLE-NUT OIL. (DE NEGRI.)

	Oil Extracted by	
	Ether.	Petroleum Spirit.
Specific gravity at 15° C.	0·926	0·921
Solidifying-point	– 18	Still fluid
Melting-point of fatty acids	20 to 21° C.	—
Saponification value	187·4	184·9
Iodine value	139·3	142·7
Refractometer (Zeiss)	—	75·5 to 76

Samples of lumbang oil and nuts from the Philippines and Hawaii were examined at the Imperial Institute. The Philippine nuts contained 33 per cent. of oil and the latter 31 per cent.

TABLE SHOWING THE CONSTANTS OF PHILIPPINE AND HAWAIIAN OIL.

	Philippine Oil.	Hawaiian Oil.
Specific gravity at 15·5° C.	0·9293	0·927
Refractive index at 20° C.	1·4772	1·4783
Iodine value, Hanu's test	155·3	161·6
Saponification value	192·1	192·6
Insoluble fatty acids per cent.	92·5	92·47
Unsaponifiable per cent.	0·51	0·83

De Negri's colour reactions were undecided. The constants for candle-nut oil are similar to those from wood oil and from a candle-nut oil examined by Lach, probably a mixed oil from different varieties of *Aleurites.* When exposed to sunlight for 25 days in a sealed tube the above oils remained fluid, whilst expressed wood oil solidified under the same conditions. Wood oil extracted by solvents, according to De Negri, does not solidify under the action of sunlight, only the expressed oil. The polymerised substance from the expressed oil melts at 32° C., the iodine value falls from 159 to 154. When heated for 100 hours in the dark at 100° C. it does not change, but on cooling remains liquid. Candle-nut oil extracted by carbon disulphide CS_2 similarly treated always remains fluid, whilst wood oil also extracted by CS_2 solidifies.

Fendler in 1903 examined the seeds of the candle-nut tree *Aleurites Molucanna* from the then German Cameroons. The kernels contained the usual normal percentage content of oil, viz. 64·4 per cent. The ether-extracted oil is yellow and has an acrid taste. Its specific gravity at 15° C. is 0·9254, its solidifying-point was –15° C. Its saponification value was 194·8, iodine value 114·2. The Reichert-Meissl value was 1·2. The solidifying-point of the fatty acids was 15·5° C. and their melting-point 18° C. The iodine value is far too low for genuine candle-nut oil. And yet, according to Fendler, the oil dries quickly when spread in a thin layer and exposed to the atmosphere.

Summary.—Henry A. Gardner gives an account of candle-nut oil, or, as he terms it, Lumbang oil, in circular (No. 41) issued by the Educational Bureau of the Paint Manufacturers' Association of the United States. This account may well be taken as the source of a brief summary of our present knowledge.

"Lumbang oil is obtained from a tree (*Aleurites Moluccana*) allied to the tung tree (*Aleurites Fordii*), which is indigenous in Polynesia, and is now cultivated largely in parts of Asia and in tropical islands such as Hawaii and the Philippines. The tree grows to a moderate height, i.e. 30 to 40 feet, and is covered with large glossy leaves. It bears two crops of nuts, which are enclosed in very thick, hard shells. The kernels are pale, and contain so much oil that they are used as a source of illumination, hence the name—'candle nuts'. They have a pleasant taste somewhat resembling Brazil nuts, and yield an oil very similar to tung oil, except that it does not gelatinise on heating. The oil has purgative properties. The pressed cake is useful as a fertiliser, and is used for this purpose by the natives, its price being $100 per ton, whereas ground fish manure or tankage fetches only $25. At the present time the nuts are shelled by hand labour, no machine having yet been invented to do this in a satisfactory manner. The average weight of the nut is 11·7 grammes, percentage of shell 67·9, and kernel 32·1, and content of oil 60·3 per cent.

PHYSICO-CHEMICAL ANALYSIS OF CANDLE-NUT OIL (GARDNER).

Specific gravity	0·927
Acid number	1·3
Saponification number	192·3
Iodine number	162·0
Refractive index	1·475

ANALYSIS OF CANDLE-NUT OIL CAKE (GARDNI

	Per Cent.
Nitrogen	7·34
Phosphoric acid (P_2O_5)	3·95
Soda (Na_2O)	0·47
Potash (K_2O)	1·42

The Lumbang Nut Industry in the Philippines.—According A. W. Prautch, of the Philippine Bureau of Agriculture, lar quantities of lumbang nut are allowed to rot under the trees owing to the want of collectors, lack of transportation, and absence of organisation for dealing with the material. "The lumbang tree grows extensively in many parts adjacent to Manila, and from time to time the nuts are gathered in a haphazard fashion by the natives. A certain amount find their way to the four local mills through the agency of Chinese traders, but when these have obtained sufficient for their needs collection ceases. It is difficult to obtain precise data as to the amount of lumbang nuts treated, but it is estimated that the total quantity will not amount to more than 100,000 piculs (1 picul = 139½ lb.) annually, and the price at which they are sold in Manila varies from $3 to $7·50 per picul for the shelled kernels. It is stated that there are two varieties of lumbang nuts, the one, a hard-shelled variety, being the true lumbang from *Aleurites Moluccana,* also known as *triloba,* the other, a soft-shelled variety, from *A. trisperma.* The latter appears to be the more valuable of the two, as the oil resembles Chinese wood oil so closely that it is difficult to differentiate them, besides which it dries much more quickly than that from the *Moluccana* species. During the last few years experiments in the planting of the lumbang tree have been inaugurated, and since 1915 the Bureau of Agriculture have distributed 100,000 seeds. The trees already growing have, however, been depleted either in clearing the ground for cultivation or for use in the manufacture of match splints, for which, the wood being soft, it has been found quite suitable. It is pointed out that anyone taking up the question of exporting lumbang should not lose sight of the fact that the nuts consist of one-third kernel and two-thirds shell, which means high freight charges for the unshelled material."

Cordemoy tells us that "in Cochin-China, Indo-Chinese lacquer, i.e. Cay lacquer, is mixed with wood oil (from a dipterocarpous tree. More likely it is the real Chinese oil that is used and not gurjun balsam) in the proportion of 2 parts of lacquer to 1 part of wood oil. The mixture is first exposed to the sun to give it the necessary fluidity. It is then passed through a sieve to free it from extraneous matter. Purified in this way it forms a very brilliant varnish. According to a note published by the 'Revue Coloniale' of 19 May, 1895, candle-nut oil (*Aleurites Moluccana,* Wild), after having been reduced by boiling possesses analogous properties to a quick-drying oil of Chinese origin, and which the Chinese of Cochin-China use in making their varnish. Specimens of wood varnished with lacquer collected in the forests of

Tayninh and candle-nut oil are, it would appear, deposited at the Saigon Chamber of Commerce. Now the oil used in China for this purpose is extracted from the seed of a tree which is no other than an *Aleurites*—*A. cordata*, Stend (*Elaeococca verrucosa*, A. Juss), that the Chinese call Tong Tse Chou or Oil Tree, and the Japanese Wu Lung. It is not therefore surprising that candle-nut oil from an allied species should have analogous drying properties and should be capable of being utilised in making these varnishes. Moreover, according to Lemarie ('Rev. Cult. Col.,' 5 September, 1899), the *Aleurites cordata* grows wild in the forests of Tonkin. It is the Cay Trau or rather the Cay Dan Son of the Annamites. But the colonists of Tonkin confuse it with the *A. Moluccana*, under the name of candle-nut tree, a name which only belongs to the latter species. Moreover, trau oil has many analogies with candle-nut oil. It is yellowish, viscous, combustible, and much more quick drying. It is used with the lac after boiling. It is the wood oil of the Anglo-Chinese market, and not to be confused with gurjun balsam."

The above statement by Cordemoy and the statement as to the drying properties of candle-nut oil by Andés which would make it out to be a better drying oil than wood oil, led the author to write to the Kew authorities to see, *inter alia*, if they could explain how it came to pass that candle-nut oil was reported as a poor drying oil on the one hand, and as one of the best drying oils known on the other. The following extract contains that part of the Director's reply which bears on candle-nut oil:—

Extract from a Letter to the Author from the Director of Kew Gardens of 16 *March*, 1917.

"On the subject of your difficulty in reconciling certain statements that have been made with regard to the properties of candle-nut oil and the possibility of a confusion between *Aleurites cordata* and *Moluccana*, and in compliance with your request for data that may b available for the purpose of removing the difficulty, I beg to enclo a memorandum containing references to the more recent literatu on the subject. Perhaps the difficulty you have experienced is n confined to the possibility of a confusion between *A. cordata* and *Moluccana*, but may be aggravated by the confusion which has pr vailed between *A. cordata* and *A. Fordii*, the latter being the tr source of Chinese wood oil."

The greater part of the memorandum referred to here is repr duced in the section dealing with wood oil.

The remarks in the memorandum relating more especially candle-nut oil are as follows:—

"*Aleurites Triloba*, '*Candle-nut*'.

In addition to the commercial products of India referred to Mr. McIntosh's letter, some particulars together with an analy of the seeds will be found in 'Bulletin of the Imperial Institute,' No. 2, 1907, pp. 135-6 (John Murray, London); 'Pharmacographica Indica,' by Dymock, Warden, and Hooper, vol. iii., pp. 278-81 (Kegan Paul, Trench, Trubner & Co., Ltd., London, 1893); and in the 'Agricultural News,' Barbadoes, 6 October, 1906, p. 317 (Dulau & Co., 37 Soho Square, London)."

Funtumia Kicksia Africana Oil is obtained from the seeds of the plant formerly known as *Kicksia Africana*, but now termed *Funtumia Elastica*, a West African rubber-bearing tree, cultivated in Trinidad and other West India Islands. The seeds are very small, 100 of them only weigh about 75 grammes. Hebert obtained 20 per cent. of oil, Rideal and Acland 31 to 33 per cent. The oil deposits a solid stearine on standing—specific gravity at 15° C. (59° F.); saponification No. 185; iodine No. 138; refractive index at 15° C. 1·4788; the insoluble acids amount to 95·1 per cent. (Rideal and Acland).

Hemp-seed Oil is expressed from the seed of the hemp plant (*Cannabis sativa*), a plant belonging to the family of *Urticaceæ*, the nettle family, and from the fibres of which cordage, ropes, etc., are spun. There is sometimes a difficulty in getting linseed absolutely free from adulteration with hemp-seed oil. This is owing to the practice of growing linseed and hemp-seed as mixed crops. The oilcake is used as a feeding stuff for cattle. In the U.S.A. the yield of hemp-seed is said to be 20 to 40 bushels of seed to the acre. The plant requires to be harvested before becoming quite ripe owing to liability to seeding. The fruit of the plant is nut-like in form, and comes on the market freed from its outer capsule. It is of an oval shape, 3 to 4 millimetres long and 2 millimetres broad, somewhat drawn together in the middle. The outer shell is brown or greenish-brown in colour, thin and hard, with a smooth surface, composed of two sections, of which the outer is pale greenish, and the inner brown-green. The fruit-like seed has a thin light green skin, and fills the capsule completely. The seed has a peculiar smell, a mild oily taste, and contains 30 to 35 per cent. of a pale limpid oil.

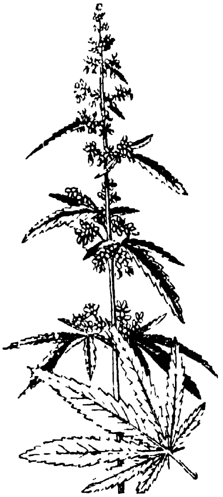

FIG. 105.—*Cannabis sativa.* The source of hemp-seed oil.

The oil is obtained in the usual way by pressing the seed with or without previous heating, or by extraction in the customary form of apparatus.

The yield of oil is about 25 per cent. by expression or 30 to 32 per cent. by extraction.

Cold pressure extracts of a thin pale green oil, warm pressure a dark thick oil.

The following figures give an idea of the composition of the seed:—

TABLE SHOWING THE COMPOSITION OF (1) GERMAN AND (2) RUSSIAN HEMP-SEED.

	German Hemp-Seed.	Russian Hemp-Seed.
Organic matter	54·30	54·95
Proteids (included in above)	(1[illegible]·95)	(15·00)
Ash	3·45	4·50
Water	8·65	9·13
Oil	33·60	31·42

In Poland, Galicia, and Russia large quantities are produced and used in the oil and varnish industries. In Russia the best sorts are used as edible oils.

The principal application of the cold-pressed oil is in cooking and baking, and large quantities of warm-pressed oil are used for burning and in the manufacture of soap.

The green soft soap of North Germany is a hemp-seed oil soft soap.

The seed loses its germinating power very quickly, hence the stock of seed should be one season old only. It is said Russia annually produces half a million tons of hemp-seed.

CHEMICAL AND PHYSICAL PROPERTIES OF HEMP-SEED OIL.

	Density at 15° C.	Solidification-point.	Saponification Value.	Iodine Value.[1]	Maumené's Test, ° C.	Oleo refractometer.
Allen	0·925-0·931	Thick at − 15° C.	—	—	—	—
Benedikt	—		—	157·5	—	—
Château	0·9270		—	—	—	—
De Negri and Fabris	0·9280	solidifies at − 27° C.	192·8	140·5	95-99	—
Fontenelle	0·9276		—	—	—	—
Hübl	—	—	—	143	—	—
Jean	—	—	—	—	—	+ 30
Massie	0·9255	—	—	—	—	—
Maumené	—	—	—	—	98	—
Shukoff	—	—	192-194·9	157-166	—	—
Souchere	0·9255	—	—	—	—	—
Valenta	—	—	193·1	—	—	—
Fahrion	0·925	—	190-5	145-66	—	—

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[1] F. Ludwig, average of 11 samples, 149·4.

FATTY ACIDS.

	Melting-point, °C.	Solidification-point, °C.	Mean Molecular Weight.	Iodine Value.	Acetyl Value.
Benedikt and Ulzer	—	—	280·5	—	7·5
De Negri and Fabris	17-19	14-16	—	141	—
Morawski & Demski	—	—	—	122-125·2	—
Hübl	19	15	—	—	—

The colour of freshly pressed hemp oil is greenish-yellow; that extracted with carbon disulphide is brownish-yellow, while ether-extracted oil is an intense fresh green. The green colour of the freshly-pressed or ether-extracted oil leaves it after some time and the oil becomes brownish-yellow. The smell and taste are like those of the seed. The flavour is described as disagreeable, the odour as mild. With regard to viscosity, at 15° C. the oil flows 9·6 times more slowly than water, and at 7·5° C. it flows 11·6 times. Hemp oil dissolves in 30 parts of cold alcohol and is miscible in all proportions with boiling alcohol, but the solubility in alcohol of any oil is a function and factor of the free fatty acid. Its solution in 12 parts of boiling alcohol deposits stearine on cooling. One part of the oil requires 2 parts of ether to dissolve it. The liquid fatty acids contain a large proportion of linolic acid, and smaller quantities of linolenic and isolinolenic acids, also oleic acid. The elementary composition of hemp oil according to Mulder is—

Carbon	76·05 per cent.
Hydrogen	11·35 ,,
Oxygen	12·60 ,,

The percentage of solid fatty acids in a hemp-seed-boiled oil separable from the mixed fatty acids was found by Lidoff to be 4·8 per cent. Fluid hempolic acid would appear to be identical with linolic acid, $C_{16}H_{28}O_2$. Hazura gave in his first research the old formula, in his second research $C_{18}H_{32}O_2$, with the hexabromlinolenic acid, of m.p. 177° C., and the tetrabromhempolic acid, $C_{18}H_{32}Br_4O_2$. Lastly, systematic oxidation with $KMnO_4$, shows that hempolic acid is not a simple body, it yields 4 per cent. of dioxystearic acid, 24 per cent. of sativic acid, and 2·5 per cent. of linusic and isolinusic acid. Fluid "hempolic" acid in addition to linolic acid, 70 per cent. contains oleic acid, $C_{18}H_{34}O_2$, about 15 per cent., and linolenic acid, $C_{18}H_{30}O_2$.

Mulder found palmitin and stearin. Lewkowitsch denies the presence of the latter. The flash-point of hemp-seed oil is 275° C. (527° F.) (Rakusin). The dextro-rotary polarisation is 0·1.

There are a number of colour tests for hemp oil. On heating with soda lye (specific gravity 1·340) it gives a brownish-yellow hard soap, whereas linseed oil gives a yellow but softer soap. With sulphuric acid an intense green coloration, similar to that obtained with linseed oil, characterises it. When 5 parts of hemp oil are mixed with part of a mixture of equal parts of strong sulphuric acid, fuming nitric acid and water, a green colour is obtained which soon turns black, and becomes reddish-brown after 24 hours' standing. Strong hydrochloric acid turns fresh hemp oil grass-green, and older oil yellowish-green.

The drying power of hemp oil has been stated to be as good as that of linseed oil. But it is far from being so. Weger in fact found it took 4 to 4½ days to dry with the oxygen absorption of 13·6 and 13·4 respectively. Hemp-seed oil is, however, a useful raw oil for oil boiling. Its green coloration can be bleached by fuller's-earth. Moreover, it may be changed to a golden-yellow by long heating at 300° F., when a golden-yellow stand oil is obtained.

When mixed with 2½ per cent. of powdered litharge and 1¼ per cent. of sugar of lead and heated, a very good boiled oil for painting purposes results. Zinc white ground with this boiled oil and painted on tin dried in 12 hours. When the price of linseed oil is compared with that of hemp-seed oil, it will be seen that if the latter will give as satisfactory results in practice as linseed oil does, its use would be profitable.

Experiments in Boiling Hemp-seed Oil.—Hemp-seed oil was first heated without the addition of driers. The temperature rose quickly to 200° C. (392° F.) without any scum forming on the surface, and with only slight formation of bubbles. Vapour with a faint, rather pleasant odour then began to be evolved, and when 270° C. (518° F.) was reached there was no "breaking" or separation of mucilage as with linseed oil. The tint of the oil on cooling was, when seen in bulk, slightly darker and perhaps a little less transparent, but the smell did not differ from that of the raw oil. By continued heating at 270° C. (518° F.) a very unpleasant vapour was evolved. On cooling, a slight increase was noticed in the viscosity, but the colour was only slightly darkened. Heated for 2 to 2½ hours at 300° C. (572° F.), a very thick-flowing golden-yellow "stand" oil of high transparency was obtained, which resembled linseed "stand" oil in smell.

A fresh sample of hemp-seed oil was treated with litharge. 500 grammes were taken, and heated to 150° C. After 10 minutes at this temperature, 40 grammes of powdered litharge was stirred in, little by little. The addition made the oil froth a good deal, but only a slight scum was formed. The colour altered to dirty greenish, darkening little by little until the product finally became brown.

A. Lidoff examined two Russian hemp-seed boiled oils with the following results:—

	I.	II.
Acid value	13·1	12·7
Saponification value	201·0	—
Hehner value	93·4	92·9
Iodine ,, ...	140·0	—
Acid value of fatty acids	148·6	152·8
Iodine value ,, ,, ...	149·1	153·4

Lidoff was astounded at the high iodine number of the fatty acids; for in the literature Morawski and Demski's figures are given as 122 to 125·7. These figures are much too low, being due to the prolonged heating of the fatty acids. Lidoff's figures for the two boiled oils for similar reactions, showing a relationship between the iodine and oxidation figures, is excessive; then the Hehner value of 93·4, and the iodine number of 140 of boiled oil I. calculated for the fatty acids themselves, give the iodine number of 149·9, which agrees well with that found by Lidoff 149·1. The acidity of the boiled oil has increased one-fourth. The increase is due to the great heat utilised in oil-boiling, as Lidoff only found the small glycerine content. The glycerine therefore plays an important rôle during the drying process, as Lidoff found by two oxidation experiments with boiled oil II., and the fatty acids contained therein. But the film was far too thick. That the layer of free fatty acids absorbed more oxygen, but took much longer to dry than the glyceride, is not surprising. Mulder obtained the same results with linseed oil. The acid value of the fatty acids submitted to the experiment (inner half 75 days, 153·4 to 163·2). Petroff made two similar experiments but with much thicker coats, one with the raw oil, the other with the same hemp-seed oil blown and heated to 200° to 250° C. (= 392° to 482° F.) for 4 hours. The oxygen absorption in both cases was 12 per cent., that of the inner half only 0·3 in 75 days. Petroff concludes that the blowing of hemp-seed oil is beneficial. These hemp-seed boiled oils took the following time to dry:—

Raw hemp-seed oil			8 days
,, ,, ,, with	2 per cent.	MnR	25 hours
,, ,, ,, ,,	2 ,,	MnL	25 ,,
Blown hemp-seed oil, ,,	2 ,,	MnR	20 ,,
,, ,, ,, ,,	2 ,,	MnL	34 ,,

Boiled Hemp Oil. Specification for South Russian Foot Plys.—Boiled hemp oil must be pure with no foots, without any bitter taste, and be unmixed with other cheap oils. It should not yield over 1 per cent. of foots. (1) It should mix easily with pigments and flow easily with the brush, dry to the bottom surface in 24 hours, and not creep. (2) The specific gravity at 15° C. must be between 0·935 and 0·955. (3) If it is agitated with strong sulphuric acid and does not take on a clear green colour but one of a reddish tinge, then there is certainly a mixture of train oil present. (4) If when mixed with ether it yields a dark red colour when poured on ultramarine, rape oil is present. (5) It must not contain a mixture of linseed oil

Horned Poppy Oil.—The oil of *Glaucium flavum* is present in the seed up to 30 per cent. of oil. When extracted in the cold it is a pale yellow, inodorous, insipid, its density is uncertain. Cloez gives for two tests 0·913 and 0·92416, one of which, evidently the first, must be a misprint. When hot expressed, this oil is darker and smells more strongly. It dries very well and should be utilised as an edible oil, and as an illuminant. As the plant springs up naturally on waste gravelly ground, on the seashore, and the banks of streams, it has been thought to multiply it there and thus render barren land profitable, such as the shingle of the lower Seine. This project was never executed.

Kaya Oil.—This oil is obtained in Japan from the seeds of *Torreya nucifera S. et Z.* (*Taxaceæ*). The plant grows wild in mountainous regions in several districts of Japan. The kaya seed is usually of a long oval shape with pointed ends. It is 1·5 to 2·5 centimetres long, and weighs on an average 1 gramme. The testa has a brick-brown colour, and is very hard; the nucleus is pale yellow, covered with reddish-brown tegmen. A sample consisted of 32 per cent. testa and 68 per cent. nucleus. The analysis of the nucleus gave the following results:—

Locality.	Moisture.	Oil.	Ash.
Tokyo	5·04 per cent.	51·07 per cent.	2·20 per cent.
Shiga	2·67 ,,	51·70 ,,	2·29 ,,

The oil is prepared by steaming and pressing the powdered seeds. About 13 per cent. by volume of the oil is obtained from the seed. For the examination of the oil, a cold drawn oil from the Tokyo seeds and two commercial specimens from Miyé and Tottori prefectures were used. The oil obtained by cold pressing is a light yellow liquid with a faint odour and mild taste. When cooled down even to − 20° C. it gave no turbidity. The commercial oils are yellow in colour, and have faint, resinous odour. Their taste is decidedly unpleasant. The Tottori oil was very turbid from the presence of admixed impurities.

PHYSICO-CHEMICAL CONSTANTS OF KAYA OILS.

	Tokyo Oil.	Miyé Oil.	Tottori Oil.
Specific gravity at 15° C. . . .	0·9238	0·9233	0·9244
Acid value	1·48	4·24	12·66
Saponification value . . .	188·38	188·34	187·95
Iodine value (Wijs)	142·21	137·95	133·37
Hehner value	95·7	—	—
Reichert-Meissl value . . .	0·93	—	—
Refractive index at 20° C. . .	1·4770	1·4760	1·4757

Kaya oil dissolves readily in the common solvents; in Valenta's test the cold-drawn oil gave turbidity at 62° C. By the elaidin test (at 15° C.) no solidification was observed after 2 hours, and at the end of 24 hours only a small deposit of a buttery substance was formed. The mixed fatty acids obtained from the cold-drawn oil form a pale yellow liquid at the ordinary temperature; when cooled, crystalline deposits were formed, which melted into the oily part at 25° C. The following constants were determined: Specific gravity (at 98° C.), 0·8509; neutralisation value, 192·81; mean molecular weight, 290·96; iodine value (Hübl), 149·45. When heated in a thin layer at 100° C. for 3 hours kaya oil dries to an elastic film. The boiled oil prepared by heating the oil with manganese borate or rosinate, dries perfectly in 24 hours at the ordinary temperature. By the hexabromide test no precipitate was obtained. The composition of kaya oil has not yet been fully ascertained. T. Kametaka obtained a tetrabromide of m.p. 114° C. by brominating the mixed acids in glacial acetic acid; so the presence of linolic acid should be taken as proved. Kaya oil belongs to the group of drying oils. Its drying property is, however, much weaker than that of linseed oil, as might be expected from its iodine value. The cold drawn oil is used as an edible oil; commercial oils have sometimes a very unpleasant resinous odour, and are utterly unfit for foodstuff. Besides for burning, the oil is used in the manufacture of oil papers, as an insecticide, etc. It may be also used as a material in the manufacture of paint and varnish.

Lallemantia Oil.—French, *Huile de Lallemantia;* German, *Lallemantiaöl.*—Density at 20° to 21° C. 0·9336; solidifies at − 35° C.; Hehner value, 93·3; Reichert value, 1·55; saponification value, 185; iodine value, 162·1; melting-point of fatty acids, 22·2° C.; solidification point of fatty acids, 11° C.; iodine value of fatty acids, 166·7. This oil is extracted from the seeds of *Lallemantia Iberica,* Fisch et M., a plant belonging to the *Labiatæ,* growing wild in the Caucasus, and cultivated as a farm crop in Russia, near Kieff. Its iodine value is very high, thus ranking it amongst the first members of the drying oils. Wood oil, however, surpasses it, although the drying properties of linseed oil would appear, according to Richter, to be inferior to it. Richter spread a little of the oil on a watch-glass, and after 9 days' exposure it dried to a thick resinous coating. But the drying properties have possibly been overrated, and confirmatory results are necessary. By heating the oil to 150° C. (302° F.) for 3 hours complete drying took place after 24 hours. The oxygen absorption by Livache's test was 15·8 per cent. after 24 hours, and for the mixed fatty acids 14 per cent. after 8 days. Ten grammes of the oil at 18° C. treated with 2 grammes of concentrated sulphuric acid gave an increase in temperature of 120° C. (248° F.) identical with a good linseed oil.

Madia Oil is extracted from the seeds of *Madia Sativa,* a Chilian plant introduced in the early decades of last century into the agriculture of the drier parts of Europe. Madia oil expressed without heat is transparent, yellow, odourless (Lindley), endowed with a peculiar odour, and fit for salads. Its cake is good for cattle. It produces in dry climates as much oil per acre as poppy. In comparison with colzas as 32 to 28, linseed oil as 32 to 21, and olives as 32 to 16. This oil dries very well and can compete with the best poppy-seed oil. The density of the oil is about 0·92922, is coloured red by nitrous acid, and forms with soda a hard colourless soap.

PHYSICAL AND CHEMICAL CONSTANTS OF MADIA OIL.

Authority.	Density at 15° C.	Solidification-point.	Saponification No.	Iodine No.	Maumené Test.
De Negri and Fabris	0·9285	- 12 to - 15	192·8	117·5-119·5	95-99° C.
Hartwich . . .	0·926-0·928	—	—	—	—
Biegler . . .	—	- 22·5 (cold drawn)	—	—	—
Winkler . . .	0·9286	- 10 to - 17 (by hot pressure)	—	—	—
Fatty Acids.	Solid-point.	Melting-point.	Iodine No.		
De Negri and Fabris	26-22	23-26	120·7		

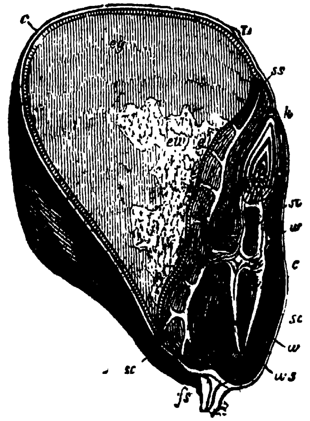

FIG. 106.—Longitudinal section of fruit of *Zea-Mais* (× 6).
c, pericarp; *n*, remains of the stigma; *fs*, base of the fruit; *eg*, hard yellowish part of endosperm; *ew*, white softer portion of endosperm; *sc*, scutellum (cotyledon) of embryo; *ss*, its apex; *e*, its epidermis; *k*, plumule; *w* (below), the main root; *ws*, sheath covering main root; *w* (above), lateral rootlets springing from the first internode of the stem, *st*. (After Sachs.)

Maize Oil, Corn Oil.—The commercial prominence which maize oil and cake have gained during the past two decades has proved the importance of this grain as a competitor of the oil seeds as soon as the characteristics of its products were understood. Both the oil and cake have been subject to the prejudices which exist against all new products, and they have been marketable only at prices which afforded a sufficient margin of saving, as compared with the older commodities whose field they invaded, to command the attention of buyers.

Maize oil has certain characteristic properties, however, that are not at present made use of, at least, to the extent they might be. It forms a strong and elastic emulsion very quickly. It is very fluid, and remains clear, and that at a very low temperature. It does not give when chilled any precipitate until 0°, when a few gelatinous strings separate. It is susceptible of refining to a handsome, almost water colour, much finer than can be done with linseed oil. Rancidity rarely or never gives trouble in this oil, nor is the danger of spontaneous combustion (ignition) so great as in others. The taste and odour can be largely removed, nor are they unpleasant in the crude oil, consisting simply of an intense maize taste and odour.

The crude oil, obvious without any test, would seem to indicate that there are great possibilities for a carefully refined product which would give it a prominent place among the edible oils, and would possibly enable it to find its way into industrial uses for which it has not thus far been suggested. It is less likely, apparently, to invade the domain of linseed oil than it is to compete with the semi-drying class to which it more distinctly belongs.

As is generally known, the oil is now made wholly from the germ of the maize kernel, which is an otherwise valueless if not, indeed, detrimental constituent of the corn, in the manufacture of glucose, starch, and in alcohol distilling. This has proved an unfailing and cheap source of supply, and this is said also to give to the cake a superiority over cake from seeds which yield a larger percentage of husk or other exterior hull. Analysis of corn cake, the figures given being percentages:—

TABLE GIVING COMPARATIVE ANALYSIS OF MAIZE, LINSEED, AND COTTON-SEED OILCAKES.

	Maize Oilcake.	Linseed Oilcake.	Cotton-seed Oilcake.
Moisture	9·75	9·50	9·1
Protein	21·70	32·75	45·0
Fat	10·50	10·50	10·0
Non-nitrogenous extract and fibre .	54·68	42·00	29·0
Ash	3·37	5·25	6·4

The larger percentage of protein in cotton-seed oil cake is the average of a series of analyses, the range of which was from 41 to 53 per cent. A careful determination of the fertilising value of the different cakes has not been made. However, they serve to indicate that corn cake is, as it would seem necessarily to be when we consider that it is made wholly from the heart of the kernel, a less formidable competitor of the oil seed product than is the oil itself.

Manihot Oil.—Manihot Glazowii oil is the product of a rubber-bearing tree, indigenous to arid regions of Brazil but cultivated in East and West Africa. The nut weighs about 0·5 gramme, about ·8 grammes, the shell or husk is hard. The seed contains 45·3 per cent. of kernel and 54·7 per cent. of shell. But Fendler and Kuhn found 25 per cent. of kernel. The whole seed yielded 15·75 per cent. of oil. On exposure to air in thin film this oil dries to a skin after a few weeks but the absorption of oxygen is not great, amounting only to 8·8 in 7 days. Specific gravity at 15° C., 0·9238 to 0·9258; m.p. below - 17° C.; saponification No., 188·6 to 189·1; iodine No., 135 to 137; refractive index at 15° C., 1·475. Fatty acids: The oil contains 95·1 per cent. of insoluble fatty acids. Specific gravity at 25° C., 0·8984; solidification-point, 20·5° C.; m.p., 23·5° C.; neutralisation No., 197·6; iodine No., 143·1.

Nsa-Sana.—Some seeds from the Calabar district of Southern Nigeria were examined by the Imperial Institute. No information was received as to the botanical source of the seeds, but from inquiries by the principal Forestry Officers, they are the product of *Ricinodendron africanum.* The sample consisted of about 3½ lb. of the seeds, which were in fair condition on arrival. They contain 45·2 per cent. of oil, which dried in a day on exposure to air at the atmospheric temperature, and left a wax-like residue. The oil has been examined chemically and found to resemble t'ung oil (Chinese wood oil) in composition. The following table gives the results obtained in the examination of the oil from the Nsa-Sana seeds and also the t'ung oil for comparison:—

	Oil from Nsa-Sana Seeds.	T'ung Oil.
Specific gravity at 20° C.	0·9320	0·933 to 0·942 (at 15·5° C.)
Saponification value	191·6	190-197
Iodine value, per cent.	147·7	149-165
Hehner value (percentage of insoluble fatty acids)	95·2	96·3
Titer test (solidifying-point of fatty acids)	35·7° C.	37·1 to 37·2° C.

These results, and the behaviour of the oil on drying, seem to show that the oil from Nsa-Sana seeds could be utilised as a substitute fo tung oil; but technical trials would be necessary in order to determine this point. Tung oil is principally sold in the United State of America, but there is also a fair market in this country, where i is used in the manufacture of linoleum and also varnish-making. Th price of tung oil in London at the date of report was from £32 to £3 per ton. The Nsa-Sana oil could also be utilised for making sof soap, and at present it would be worth from £18 to £20 per ton fo this purpose. The value of the seeds would be determined by th amount of oil which they contain and the price obtainable for it. The seeds were analysed, and the results showed that the "cake" left after the extraction of the oil would possess a feeding value approximately equal to that of decorticated cotton-seed cake. The meal was examined for poisonous constituents, and indications of the presence of an alkaloid were observed. On this account, and also owing to the nature of the oil which the seeds contain, it seems improbable that the cake could be used as a cattle food, and very careful experiments as to its effects on animals would first have to be made before it could be recommended for this purpose. It could, however, be utilised as a manure, since it is rich in nitrogen.

Manketti Nut Oil (*Nsa-Sana Oil*).—This oil is said to be the product of *Ricinodendron Rhautanenii* (Schinz), belonging to the family of Euphorbiacea or Sporge Worts, growing to a height of 40 to 50 feet, and common in the South African veldt, indigenous to South-West Africa. But the same tree apparently grows in Central Africa, if we may take Southern Nigeria as part of the Central Division of Africa. At any rate the fruit of the *Ricinodendron Rhautanenii* is described as weighing about 10 grammes, and the seed about 1¼ grammes. The kernel weighs about 10 per cent. of the whole fruit. It contains 51·5 per cent. of oil = 32·3 on the whole seed, or 5·15 per cent. on the fruit. A later bulletin describes the fruits as ¾ to 1 inch in diameter, and 1 inch to 1½ inches in length, consisting of husks 13 per cent., mesocarp 20 per cent., and nuts 67 per cent. The kernel of the nut formed 10 per cent. of the entire fruit. The kernels contained about 4·1 per cent. of moisture and 57·2 per cent. of a bright yellow liquid oil, giving the following numbers: specific gravity at 20° C. 0·9320; acid number, 1·9; saponification number, 191·5; iodine number, 133·6. Its iodine number, insolubility in alcohol and solubility in light petroleum, point to the oil being semi-drying and not to its belonging to the castor-oil group. It is not particularly suited for paint-grinding or varnish-making. It is used as an edible oil. The small proportion of kernel and the difficulty of extracting the oil debar as unprofitable the exportation of nuts to Europe.

With regard to Manketti nuts, the latest information states that these are obtained from a Euphorbiaceous tree (*Ricinodendron Rautanenii*), which grows on the South African veldt. It is a moderate-sized tree growing to a height of 15 to 25 feet, in some places forming extensive forests. The fruits are about ¾ to 1 inch in diameter and 1 to 1½ inches long, have a tough outer reddish-brown husk, a pulpy brownish mesocarp, and a nut which amounts to about 67 per cent. of the whole fruit. The shell of the nut is thick and woody, while the kernel, amounting to only 10 per cent. of the whole fruit, is oily and cream-coloured. The kernels yield 57·2 per cent. of a bright yellow oil, which has an iodine value of 133·6 and is a semi-drying oil. This could be used for soap-making and possibly as an edible oil, but for paint and varnish purposes it would not be altogether suitable. At the present time the kernels would fetch perhaps £20 per ton, but in ordinary times their value would be nearer £12 or £14. The nuts are extremely difficult to crack, and this, together with the small proportion of useful kernel and mesocarp, is regarded as a barrier to their employment in preference to other oil seeds as long as the latter can be obtained at reasonable prices.

Niger, Kersanee, or Ram-til Oil.—The "Niger seed" of African commerce, and the ram-til or Kersanee of Indian cultivators is the product of a plant belonging to the natural order of *Compositæ Guizotia Oleifera*. The plant grows wild on the Gold Coast of Africa and is cultivated in Abyssinia and in many parts of India, especially Mysore and the Deccan. Here the seed is sown in July-August after the first heavy rains, the fields being simply ploughed and neither weeded nor manured. The seed is drilled in rows 11 to 13 inches apart, and 4 to 6 lb. seed per acre is held sufficient. It is commonly grown alone but is sometimes accompanied by a pulse crop. When the crop is ripe it is cut (3 months after the sowing) near the root and stacked for 8 days, and after being sun-dried for a few days, the seed is threshed out and separated from fragments of the plant by a fan, the produce being about 2 bushels an acre, which seems a very poor yield. By the common country mills only 25 per cent. of oil is got from the seed, but better appliances bring the average up to 35 or even 40, but the seed dries quickly, and in England yields only 16 gallons of oil, while rape-seed yields 20 gallons. The oil is limpid, clear, pale yellow or orange in colour, and sweet flavoured with a nutty taste, and is used as an edible oil by the poorer classes of India and commonly as a lamp oil. It is said to be useful in case of dislocated or fractured bones in cattle. Though much inferior to gingelly it is often used as a substitute for it and to adulterate both gingelly and castor oil. The oil contains little stearic or palmitic acid, hence soap made from it though very white is soft. The cake is highly appreciated in some parts of the country, being much esteemed as a food for milch cows. The seeds are crushed in Hull and Marseilles. It is used as a substitute for linseed oil when the latter is dear, and also to adulterate rape, etc., oils. It is said by Allen to dry rapidly at 100° C. From its iodine number Niger-seed oil falls to be classed amongst the slow drying. However, it is said, owing to the scarcity and high price from time to time of linseed oil of late years, o be largely used as a linseed oil substitute. On this basis Meister nade some experiments on its drying properties. He found it to lry by itself in 8 days, but by adding driers in 16 to 20 hours. But he boiled oil was much darker than boiled linseed oil, and the dried urface remains tacky for a whole day. To some extent Niger-seed il closely resembles Soya bean oil, and is only used as a substitute for ed linseed oil when the product is pale enough coloured.

For details of the extent of the different areas under this crop in e provinces of India, so far as statistics are available, and the crop classified with other oil crops, the reader is referred to Sir George Watt's "Commercial Products of India," page 625.

Oil from the Para Rubber Tree, Hevea Seed Oil.—On extraction with petroleum ether the entire seed gives 20 per cent. of oil. The kernel alone, which is about half the weight of the seed, gives 42·3 per cent. The total oil is distinguished from that of the kernels alone mainly by containing a solid fat with a high saponification number and low iodine value. The oil dries in the air to a pale transparent coat, and could be used as a substitute for linseed oil, especially now that Hevea is systematically cultivated for rubber. The kernel oil shows the following constants: specific gravity at 15° C., 0·93; free acids reckoned as oleic, 5·4 per cent., acid number, 10·7; saponification number, 206·1; iodine number, 128·3. A sample of oil from ground seeds gave 65·6 per cent. of free fatty acid reckoned as oleic. This large amount is due to a decomposition of the neutral oil in the crushed seed by an enzyme, and makes the meal useless as fodder. Nevertheless the press-cakes from the kernels can be fed to cattle. Analysis of these press-cakes gave: Water, 13·36 per cent.; ash, 5·19; fat, 6·00; protein, 26·81; cellulose, 48·64. Hevea-seed oil is valued at about £20 per ton. It is not advisable to export the whole seeds, but the kernels, which are taxed at from £10 to £12 per ton, must be exported. The press-cakes have about the same value as linseed press-cakes, viz. from £5 15s. to £6 15s. per ton.

Para Rubber Seed Kernels.—A sample of Ceylon kernels yielded 45 per cent. of oil on extraction by solvents. A sample of the extracted oil was found to give a high "acid value," and this was seen to be the cause of the poor non-spreading qualities of paint prepared from it. A high "acid value" is given by oil from damaged or old kernels; only sound seeds should be used. If seeds are decorticated on rubber plantations, as they should be for export, they should be well sun-dried, to prevent moulds, which are likely to liberate free fatty acids from the oil.

Samples of the seed were distributed to various firms for technical trial, and samples of the cake, after expressing the oil, were sent to the South-Eastern Agricultural College, Wye, for feeding trials. The results of these trials may be summarised as follows:—

1. *Paint and Varnish Manufacture.*—One of the principal uses to which the oil may be put is the manufacture of paints and varnishes, since it belongs to the class of oils known as drying oils and closely resembles linseed oil, for which it forms a good substitute for the above purposes. Manufacturers to whom the samples were sent for trial state that, unless the oil is obtained at a fairly reasonable price compared with linseed oil, it could not compete with the latter.

2. *Linoleum Manufacture.*—From several trials made with the oil, the general opinion was that it was not very suitable for linoleum manufacture, and could not be used as a substitute for linseed oil, unless the price was very low.

3. *Soap Manufacture.*—One firm of oil crushers said that it might be equal in value to linseed or cotton-seed oil for soft soap.

Conclusions.—There would be no difficulty in finding a suitable market for the oil, not only as a substitute for linseed oil, when the latter was high in price, but also for purposes for which linseed oil was unsuitable; but in the problem of utilising the oil, cost of raw material and cost of manufacture of the oil and quantities available all intervene.

By hydrogenation a new market may be found for oils of this type, e.g. in candle-making or even for edible purposes.

Pára Rubber-seed Cake: Cattle and Sheep Feeding Trials.—The first consignment of cake from Rangoon used in feeding trials was abnormal, as it contained about 18 per cent. of fat, whereas not more than 6 to 9 per cent. would be normally present in the cake from well-expressed seeds. In the second series of experiments a cake of more normal composition was used. In the first trials, which were on a small scale only, the cake was fed to cows; most of them ate the cake readily after it was moistened with water. (*N.B.*—It is dry and powdery in the natural state.) No abnormal results were obtained.

Similar results were obtained in the case of sheep, which did not like the cake fed alone, but ate it mixed with other foods. In the second series, 1½ tons of cake from kernels obtained from Ceylon were used. The cake used is stated to resemble a normal market product, and to be comparable with linseed cake used in England. The following results were obtained from these feeding trials:—

Sheep.—A group of animals accustomed to trough feeding were used, and the smallest admixture of Pará-seed cake in other concentrated food was detected by them and left uneaten, even when the total food supplied over a fortnight was reduced below the ration necessary for maintenance. All attempts at feeding sheep with the cake failed.

Young Cattle.—These ate the cake readily, but when the quantity was increased to 8 lb. per head daily, scouring occurred, and even 5 lb. per day with 56 lb. of mangold produced slight laxative effects. Further experiments confirmed these results, and the cake should not, therefore, be fed in larger quantities than this latter amount. The beef from two of these cattle, subsequently slaughtered, after having been fed with Pará-seed cake at the rate of 6 lb. per day for 10 weeks, was reported upon very favourably.

Dairy Cows.—Six barren cows were taken for this trial and were fed with increasing quantities of Pará rubber-seed cake up to 14 lb. at the end of a week, this being the only concentrated food given. No change was observed in the excreta after continuing the trial for 6 days. The yield of milk rose, as the food was richer than that normally fed, but the percentage of milk fat was unchanged. Butter made from the milk was normal. The conclusion is drawn that dairy cows may be safely fed with Pará-seed cake.

Full-grown Fattening Cattle.—The dairy cows used in the previous trial were fattened while in milk, the amount of cake fed being reduced from 14 lb. to 8 lb. with the addition of 4 lb. of other cake. The cows remained healthy and gave a high milk yield, till they were intentionally dried off a month before sale for slaughter. The increase per day in live weight over a period of 9 weeks was 1·7 lb. per cow. From these experiments the cake appears to be an excellent fattening food for cows, and its value as a cattle food has been proved.

TABLE SHOWING THE CHEMICAL COMPOSITION OF THE CAKE USED IN THE TWO TRIALS IN COMPARISON WITH LINSEED CAKE.

	Para-seed Cake (Abnormal Sample).	Para-seed Cake (Normal Sample.)	Linseed Cake.
Moisture	6·91	8·75	11·6
Crude proteins	29·93	30·19	29·5
Consisting of—			
True proteins	27·03	24·85	—
Other nitrogeneous substances	2·90	5·34	—
Fat	17·68	8·71	9·50
Carbohydrates (starch, etc.)	35·97	41·71	35·54
Fibre	4·82	5·01	9·10
Ash	4·69	5·60	5·20
Nutrient ratio	—	1·20	1·20
Food units	—	139	133

The close agreement between the normal cake and linseed cake is very marked. A small quantity of cyanogenetic glucoside was present, yielding approximately 0·02 per cent. prussic acid—a negligible quantity.

Perilla Oil is crushed or extracted from the kernel or almond of the seed of a plant belonging to the Labiatæ, *Perilla Ocymoides,* which grows in Japan, China, and India. The fresh oil is pale yellow in colour and tastes and smells like linseed oil. In a very old acid oil Meister found the colour to be very brown and the smell fishy. The oil is used in Japan for the same purpose as wood and in the Himalayas as an edible oil. The acclimatisation of the plant in Europe has hitherto been impeded by the fact that the oil is only exported to Europe in small quantities. In Japan the average annual crop of perilla seed is approximately 1,000,000 ken (1,330,000 lb.). 1,283,662 U.S. gallons of perilla oil worth $691,742, and 930,463, value $486,894, were produced in Japan in 1912 and 1913 respectively.

PHYSICAL AND CHEMICAL CONSTANTS OF PERILLA OIL.

	Observers.			Tsujimatsu.
	Wijs.	Meister.	—	
Specific gravity . .	0·9306 D^{20}_{4}	0·931	0·937	930·8 to 931·0$^{15}_{15}$
Refractive index . .	—	—	1·4780	1·4822 to 1·4855
Acid number . . .	0·9	10·9	4·3	0·846 „ 6·57
Saponification number .	189·6	192·1	193·4	189·67 „ 193·88
Iodine number . .	206·1	194·7	193·3	187·48 „ 202·45
Fatty acids— . .				
Melting-point . . .	– 5° C.	– 4° C.		
Acid number . . .	197·7	197·1		
Mean molecular weight .	284	284		
Iodine number. . .	210·6	198·2		

The iodine value given by Wijs for Perilla oil is the highest of any oil, the iodine value of which has hitherto been determined. Meister found his low absorption both by the Wijs and the Waller method, and ascribes such low results as being due to the age of his sample with an average Hehner number of 95. The calculated iodine number of the fatty acids in Wijs' sample should have been 217, and in Meister's sample 205; that in both values lower than those calculated can be readily understood.

In harmony with the lower iodine number is the fact that the melting-point of the mixed fatty acids is the lowest of any oil hitherto determined. It arises from an abnormal small content of saturated, i.e. solid, fatty acids. Fahrion not being satisfied with either Wijs or Meister's figures, and having a small quantity of Perilla seed at his disposal, extracted the oil with petroleum ether. The yield was 36 per cent., which agreed very well with Wijs' figures of 35·8. The seed was apparently pretty old. The iodine number of the oil was only 192·4. The separated fatty acids were completely fluid at summer temperature, but at 0° C. some crystalline fatty acids separated. From the high iodine value of Perilla oil we would naturally look for a more rapid drying oil than linseed oil. On this point Weger gives oxygen absorption numbers of 18·3 and 20·9, and does not regard these figures as small. He found Perilla oil showed a sort of inertia on glass plates, and tended to run into drops like quicksilver, so that it is difficult to obtain a uniform surface. Meister gives the following figures: A normal film in 6 to 8 days and a thin film 0·5 mg. per sq. cm. in 2 to 3 days, but not uniformly. Lately it has been stated that rapid heating to 250° C. completely solidifies it. Thickened Perilla oil dries off uniformly, and when boiled dries more rapidly than a similarly boiled linseed oil, as shown in the following table:—

TABLE SHOWING THE DRYING PROPERTIES OF RAW PERILLA AND BOILED PERILLA OIL AS COMPARED WITH RAW AND BOILED LINSEED OIL.

	Time of Drying, Hours.	Oxygen Absorption.
Linseed oil, raw	96	19·3
Perilla „ „ 0·8 mg. per sq. cm. . .	144	18·3
„ „ „ 0·5 „ „ . . .	60	21·2
„ „ heated to 250° C. . . .	64	18·3
„ „ „ 7 hours to 250° C. . .	48	13.4
„ boiled oil, 3p er cent. of PbMnR dissolved at 150° C.	6	21·8
Boiled linseed oil, 3 per cent. PbMnR dissolved at 150° C.	10	15·1

Perilla oil is obtained from "Perilla Nankinensis." Two lots of this seed were imported, and one lot of 666 lb. on being pressed yielded 25 gallons of oil, which it was intended should be distributed among the members of the committee on testing paint vehicles of the American Society for Testing Materials. The seed contained 33 per cent. of oil. Analyses of the press-cakes and oils are given below:—

Nitrogen	5·28
Phosphoric acid	2·58
Soda Na_2O	0·56
Potash K_2O	1·50

A Perilla oil boiled with 5 per cent. of above driers dried readily in 4½ hours, whereas boiled linseed oil takes 6 hours. From the published figures the oxygen absorption of Perilla oil sinks during oil-boiling; according to Meister, the maximum oxygen absorption of pure Perilla oil averages 25 per cent. The oil heated to 270° C. has been found to bleach pale yellow and does not darken in colour. It bleaches very rapidly with fuller's-earth. Thickened Perilla oil is used for the same purposes as thickened linseed oil, and is utilised for the manufacture of printing-ink vehicles. Perilla oil will form a very good substitute for linseed oil when it is available in suitable quantities on the market, and at a fair price.

Poppy-seed Oil.—Poppy-seed oil, so highly esteemed by artists, is obtained by crushing the seeds of the poppy (*Papaver somniferum*), indigenous to the Eastern Mediterannean countries, but cultivated generally all over the world, partly for opium, partly for the oil in the seeds. The chief producing countries are China, India, Persia, Asia Minor, Egypt, Algeria. There are two varieties of the poppy: *Papaver album*, D.C., with white seeds, and *Papaver nigrum*, D.C., with black seeds. Levant seeds are white, grey, blue, or red. Indian seeds are almost always white.

Cold-pressed poppy-seed oil has a mild, pleasant smell, it does not readily rancidify; the brown (ruddy) oil, on the other hand, has an acrid unpleasant taste, and its smell recalls linseed oil. The white poppy-seed oil of the first pressure is much used as an edible oil, either as it is—some persons prefer it to olive oil owing to its neutral taste—or in admixture with olive oil. It is also used in pharmacy in the preparation of emulsions. Second pressed oils are of a more or less dark brown colour, which hardly allows of their being utilised as edible oils. However, it is possible by appropriate treatment to give them the yellow colour of first pressure oils. Germany imported, prior to the war, 30,000 tons of poppy-seed; her own production, it was acknowledged, did not equal one-tenth of that amount.

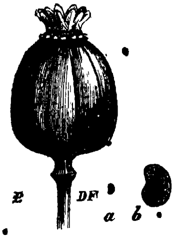

FIG. 107.—Black poppy-seed: (*a*) natural size, (*b*) enlarged.

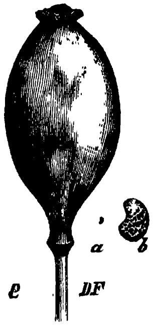

FIG. 108.—White poppy-seed: (*a*) natural size, (*b*) enlarged.

The white poppy yields the best oil, and is the seed used for medicinal purposes. The black poppy is the variety most extensively cultivated, as an oil producer being the most profitable. The yield of fatty oil has been said to be about the same in both varieties, viz. about 60 per cent. According to Sacc the poppy-seed contains:—

TABLE SHOWING THE PERCENTAGE COMPOSITION OF POPPY-SEED. (SACC.)

	Per Cent.
Oil	54·61
Protein	23·26
Albumenoids	12·00
Cellulose	6·00
Ash	2 to 3

TABLE SHOWING THE PERCENTAGE COMPOSITION OF POPPY-SEED. (LEATHER.)

	Per Cent.
Nitrogen	2·57
Albumenoid nitrogen	2·84
Moisture	4·00
Oil	48·95
Sand	2·97
Albumenoids	17·50
Soluble carbohydrates	16·99
Woody fibre	5·09
Soluble mineral matter	0·90

The commercial yield of the seed when crushed oscillates between 36 and 40 per cent., and according to Renard between 37 and 39 per cent. in the oil-crushing mills of Northern France. The oil is filtered before marketing. Poppy-seed does not contain morphine as alleged.

Extraction.—The poppy heads are opened after being partially dried, and their contents discharged on to an iron plate; they are then winnowed to remove fragments of the capsule, and afterwards ground to meal, which is packed in bags made of canvas and pressed, the oil being caught in tubs, where it is left to settle and thoroughly clarify. Two kinds of oil are on the French market: 1. The white salad oil, the oil from the first pressing of the best quality seeds. This very superior oil is also used in the manufacture of very high-class paints, such as are used by artists. This oil is almost colourless, or of a very pale golden-yellow. 2. The second quality of poppy-seed oil is used as an edible oil, in paint, and for other technical purposes it is the result of the second cold pressing. Likewise it is the result of pressing inferior seed. 3. By hot pressing a much inferior oil is got, only fit for soap-making. Poppy-seed oil is sometimes obtained by heating the seed, and mixing the products of two successive pressings In India the first pressing is done cold and the second pressing is done hot, so that expressed oil is intended in India for use in industry, rather than as an edible oil.

French Poppy Oils.—There are two chief classes of poppy oil used in France, that made from home-grown seed being termed oeillette, whilst that from imported seed is known as pavot. As the former is the more expensive, it is desirable to be able to differentiate between them; and for this purpose Vuaflart gives the following: Density, oeillette oil, 0·924 to 0·960, pavot oil, 0·923; iodine value, 133·1, 132·3; saponification value, 192, 195; oleorefractometer index, 26·6, 25·3; butyrorefractometer index at 25° C. 72·5 to 73, 71·5 to 72. There is a slight difference in flavour, the oeillette oil producing the impression of greater viscosity, though this is not borne out by the viscometer test. The greater thickness, however, is manifested by the capacity of forming a persistent froth when agitated, the fine air bubbles remaining imprisoned in the oil and rendering it opaque; whereas pavot oil under the same treatment remains clear and the air bubbles are larger. Frothing also occurs when air is blown through oeillette oil, but not with pavot oil. Oeillette oil, also, has a fine yellow colour, darker than that of pavot oil. The two may be equalised in this respect by treating the latter with a neutral chromate of potash and a trace of fuchsin. The artificial colouring, however, may be detected by the red coloration given with hydrochloric acid; and it is evident that a sample responding to this test, whilst resembling oeillette oil in colour, must be pavot oil, provided it exhibits the characteristics common to both.

The Drying Properties of Poppy-seed Oil.—Looking to its linolenic acid content, the rate of drying of poppy-seed oil is not so rapid as one would wish. It takes 6 to 8 days to dry. Cloez found in his oxidation experiments with thick films that the oxygen absorption of poppy-seed oil was the same as that of linseed oil, viz. 7·0 per cent. Mulder obtained a higher absorption than this for linseed oil. During his experiments on the plate, he reduced the thickness of the coating to 15 mg. per sq. cm. and the weight of the inner half increased 12·2 per cent. in 30 days. With two experiments in direct sunlight, with films of 3·2 to 4·2 mg. per sq. cm., he only found 4·3 and 7·6 per cent., and these were maximum figures as there was no increase from the 3rd to the 15th day. The oxygen absorption of poppy-seed oil is naturally smaller than that of linseed oil. Weger found 13·4 in 6½ days. J. Petroff made some experiments on the drying of poppy-seed boiled oil. He dissolved 2 per cent. respectively of (*a*) manganese rosinate and (*b*) manganese linoleate, in one experiment in the raw poppy-seed oil, and in the other, in poppy-seed oil blown for a long time between 200° and 250° C. (392° to 482° F.), so as to obtain a very thick oil. He found the oils took the following times to dry:—

Raw poppy-seed oil	8 days
„ „ „ with 2 per cent. MnR . . .	25 hours
„ „ „ „ 2 „ MnL . . .	34 „
Blown poppy-seed oil, with 2 per cent. MnR . . .	34 „
„ „ „ „ 2 „ MnL . . .	34 „

The thickness of the film was 3 mg. per sq. cm., so the time of drying was unduly long.

The phenomena incidental to autoxidation are not n[illegible] so strongly in evidence in the case of poppy-seed oil as in the case of linseed oil. This is borne out by the elementary composition of poppy-seed oil, given in the special literature on the subject.

Author.	Carbon, per Cent.	Hydrogen, per Cent.	Oxygen, per Cent.
Sacc.	76·6	11·6	11·8
Lefort	77·2	11·4	11·4
Cloez	77·5	11·4	11·1
Mulder	76·6	11·2	12·2

Completely dry poppy-seed oil cedes to ether about 20 per cent., dried linseed oil 27·5 to 28·6 per cent., from which Mulder inferred that poppy-seed oil contained more oleic acid, but this does not agree with his subsequent calculations, where he only estimates the oleic acid as 8 per cent. of the dried portion of poppy-seed oil which he identified with linoxin.

Hazura and Prussner obtained from 100 grammes of fluid papaveric acid 8·5 grammes of dioxystearic acid, 18·5 grammes of sativic acid, 0·3 gramme of linusic and isolinusic acid. However, they afterwards gave the unsaturated fatty acids of poppy-seed oil as:—

TABLE SHOWING THE PERCENTAGE COMPOSITION OF THE UNSATURATED FATTY ACIDS OF POPPY-SEED OIL.

	Per Cent.
Oleic acid	30·00
Linoleic acid	65·00
Linolenic acid	5·00
	100·00

All the above data requires confirmation, as well as Tolman and Munson's figures. Lately, some light has been thrown on the linolenic acid content of poppy-seed oil and linseed oil as established by Mulder by the fact which has been definitely established, viz. that poppy-seed oil has no hexabromide value.

Behaviour of Poppy-seed Oil on Storing with Access of Air.—Sherman and Falk exposed poppy-seed oil to the air in an open vessel protected from dust, and frequently shaken for several months. The following alteration in the constants took place:—

TABLE SHOWING THE ALTERATION IN THE CHEMICAL AND PHYSICAL CONSTANTS OF POPPY-SEED OIL AFTER EXPOSURE TO AIR IN BULK.

	d 15·5° C.	Acid Value.	Iodine Value.
Beginning	0·923	5·5	125·3
End	0·930	7·2	117·1

The differences between the autoxidation, as shown by the specific gravity, and the iodine value of the oxidised substance are abnormally small.

Poppy-seed oil is stated by various authorities to become very rancid. According to Utz, however, it becomes less rancid than sesame oil, and that, he asserts, is the reason that oil crushers regularly mix sesame oil with poppy-seed. Moreover, poppy-seed oil is said to split up into fatty acid and glycerine very readily. Nordlenger found in expressed edible poppy-seed oil up to 5·6 per cent. and in expressed technical oil up to 18·8 per cent.; in poppy-seed cakes, 3·7 to 6·8 per cent. of oil was found with an acid value of 86 to 140·4. Without doubt these poppy-seed cakes had undergone internal autoxidation.

Poppy-seed oil is often spoiled by sesame oil, the accidenta presence of which may be due to the fact that the poppy-seed i crushed in oil mills which are crushing sesame-seed at the same time Sometimes the presence of extraneous oils is due to wilful addition for cotton-seed oil, earth-nut oil, and linseed oil may be detected. There is no official method for the analysis of poppy-seed oil, not even in France. The first effort should be to detect any artificial coloration which might react on the reagents to be used to detect foreign oils by coloured reactions, and more particularly on those of sesame oil. In the absence of such artificial colours or after their elimination, cotton-seed and sesame oils are detected by the usual methods, i.e. by the Bellier and Villavecchia tests, after previous purification as advised by Marcelle and by Tocher for sesame oil, Halphen's test for cotton and earth-nut by the detection, and if need be the estimation, of arachidic acid. But some circumspection must be brought to bear in the detection of sesame oil. The first signs should be controlled by the use in succession of the different coloured reactions of sesame oil. The detection of sesame oil based on the determination of the iodine value is quite illusory. In the preceding tables it will be seen that the iodine value of these oils varies between 131 and 140, with an average of 136, say a difference of 7 units. The iodine value of sesame oil being 105 the substitution of 100 would produce a lowering of 31 units, say 0·31 for 1 per cent of sesame oil. It follows that in adding to a poppy oil, the iodine value of which is 140, 25 per cent. of oil of sesame, its iodine value would be lowered to the normal figure of 133. Consequently a fraud of 25 per cent. would escape the analyst. The detection of cotton-seed oil presents no difficulty, and the examination for earth-nut by the presence of arachidic acid is simplified by the fact that tests on poppy-seed oil give no arachidic acid. Linseed oil may be detected by the method given under walnut oil. Poppy-seed oil yields no insoluble derivatives.

Poppy-seed oil contains amongst its solid fatty acids both stearic and palmitic acid, and according to Mulder both lauric and myristic acids. So as to prepare the solid fatty acids, Mulder kept the alcoholic solution of the saturated fatty acids for a long time in the cold of winter, and found 13·7 per cent. separated out. On various grounds Mulder regarded this figure as far too low, and estimated the saturated fatty acids at 20 per cent. On fractional crystallisation of the solid fatty acids from alcohol, myristic acid, $C_{14}H_{28}O_2$, with a melting-point of 53·2° C., is isolated, and lauric acid, $C_{12}H_{24}O_2$, with a melting-point of 46° C. Stearic acid is not found, but a small amount of palmitic acid, with a melting-point of 62° C., is obtained after some time. At the present time it is believed that all the saturated fatty acids consist of palmitic acid, and that it is present to the extent of 6·7 per cent. as determined by Tolman and Munson, from the iodine values of the salts soluble in ether, and insoluble therein. Fluid papaveric acid behaves, according to Mulder, like a mixture of oleic and linoleic acids, but unlike linoleic acid it does not become red in the air. The dry distillation results of poppy-seed oil differ from those of linseed oil, and the distillation residue did not remain a thin fluid like the anhydride of linoleic acid. Lead papaverate diffused through ether, and when oxidised did not become red like lead linoxate; such gave on analysis strong indications of containing much less oxygen. Mulder explained that this was due to its containing much basic lead linoxate, whilst only the basic lead linoleate is soluble in ether.

Rakusin gives the flash-point of poppy-seed oil as 250° C. (482° F). Some sorts of poppy-seed oil are optically inactive whilst others are slightly dextro-rotary, up to + 0·17°. Crossley and Le Soeur have given + 4°, whilst Utz gives pure poppy-seed oil as optically inactive. Several authorities found iodine values between 130 and 140. Higher values of 140 to 160 were found by Utz, who asserts that the poppy-seed oil on the market contains as much as 40 per cent. of sesame oil. Utz extracted Indian, Levantine, and German poppy-seed with petroleum ether, and found the iodine values of the oils so obtained to be 153·5, 157·5, and 156·9. Later on, he found two commercial oils which only gave a slight sesame reaction, with iodine values between 150·6 and 151·6. Tolman and Munson for oil cold pressed from pure poppy-seed found iodine values of 133·2 and 134·9. For the inner iodine value they found 151·7, whilst Toutelli and Ruggeri found 149·6. As sesame oil has only an iodine value of 103 to 112, it naturally lowers that of poppy-seed oil. Moreover, the refraction is also lowered. Poppy-seed oil has a refraction of 78·1 to 78·4, whilst sesame oil is only 73 at 15° C. Finally, sesame oil is optically active.

The following table is due to Vuaflard, from which he concludes that poppy-seed oil, pavot, and oeillette are about similar:—

TABLE SHOWING THE CONSTANTS OF OEILLETTE AND PAVOT OILS. (VUAFLARD.)

	Oeillette.		Poppy-seed, Pavot.	
	1	2	1	2
Density at 15° C.	0·926	0·924	0·923	0·923
Iodine value	133·1	—	132·3	—
Saponification value	192	—	191·5	—
Oleorefractometer degree	26·6	—	25·3	—

By applying Bellier and Villavecchia's reagents to the samples of poppy-seed oil, the chief "constants of which are given," Royer remarks: "From experiments undertaken by himself in extracting Indian poppy-seed and indigenous poppy-seed it follows that in no case do the products so prepared respond to the reactions of sesame oil with Bellier and Villavecchia's reagent. The same was the case with oils extracted by the hydraulic press. However, oil extracted from Indian seed yielded, with Bellier's reaction, a very weak green coloration.

hose oils, responding to the sesame oil reaction, all came from oil mills hich were crushing sesame, or pavot, at the same time, which may ad one to suppose that these samples were not perfectly pure. If e admit that this phenomenon is due to these oils containing a trace f sesame oil owing to the two seeds being crushed in oil mills rushing both seeds simultaneously, then the same reaction ought to ccur with first crushed oil from the same oil mills. Now the latter o not give any coloration. A decision on this point may, therefore, e suspended." Royer also found that Bellier's green colora- ion is only given by Indian oils, second crushed country oeillette ils do not generally respond, and moreover, purified oils respond far ore readily to the test. "The tendency to yield the green coloration oils loaded with impurities is masked by others." This explana- ion, if *primâ facie* satisfactory, does not show why first crushed oils, nly slightly charged with impurities, do not give the green colour. oyer sums up his examination thus: Of the twenty-four samples f oil examined, ten responded to Bellier's test by giving a more or less ccentuated but very decided green coloration, five gave a greenish- ellow coloration, seven a yellow or orange coloration, and two a non- escript colour. If these two be calculated as giving a green colora- ion on refining, we get a total of twelve samples, 50 per cent., esponding to the sesame oil test, 20 per cent. doubtful, and 30 per ent. behaving normally with Villavecchia's and Fabris' reaction. ixteen samples, say 66 per cent., gave a rose or red reaction. Thus he use of Bellier's reagent to detect sesame oil seems more reliable han that of Villavecchia and Fabris. It cannot fail to be observed hat out of fourteen samples of indigenous oils, eight did not in any ay respond to either of these reagents or gave a weak response to he Villavecchia and Fabris test, but unconfirmed by Bellier's reagent No. 1), or conversely the more decided response to this test as egards 4 and 5 is decidedly not confirmed by the Bellier test. here are, therefore, eleven oils which present themselves normally, r almost normal, as of the two exceptions one oil is a chemically reated oil No. 1, one the anomaly of which is indicated by a brown oloration, with the Bellier test No. 2, another purified by a secret rocess, all of which leads to the belief that these tests may be utilised or the examination of country oeillette oil.

POPPY-SEED OIL. FATTY ACIDS.

	Benedikt and Ulzer.	De Negri and Fabris.	Hubl.	Thorner.
Melting-point, ° C.	—	20·21	20·5	20·5
Solidification-point	—	—	16·5	16·5
Saponification value	—	—	—	199
Mean molecular weight	279·1	—	—	—
Iodine value	—	139	—	116·3
Acetyl "	13·1	—	—	—

POPPY-SEED OIL. TABLE OF AVERAGE CONSTANTS BY SEVERAL OBSERVERS.

Observer.	Density.		Solidification-point, ° C.	Helmer's Value.	Saponification Value.	Iodine Value.	Maumené's Test, ° C.	Index of Refraction.
	° C.							
Allen	·15	0·924-0·937	—	—	—	—	—	—
Archbutt	98-99	0·8738	—	—	—	—	86-88	—
Beckurts and Seiler	—	—	—	—	—	—	—	72 at 25° C. (Zeiss's Inst.)
Clarke	15	0·9262	—	—	—	—	—	
Crossley and Le Sueur	15·5	0·9255-0·9268	—	94·97	189-196·8	133·7-137·1	—	
Dietzel and Kreszner	—	—	—	95·38	—	—	—	63·4 at 40° (Zeiss)
De Negri and Fabris	15	0·927	—	—	193·6	136·8-137·6	87-88·5	
Dieterich	—	—	—	—	197·7	137·6-143	—	—
Fahrion	15	0·924-0·927	− 15 to 20	—	—	—	—	—
Gerard	—	—	− 18	—	—	—	—	—
Hübl	—	—	—	—	—	136	—	—
Jean	—	—	—	—	—	—	—	+ 23-35
Mansfeld	—	—	—	—	—	—	—	74·5 at 25° C. (Zeiss's Inst.)
Maumené	—	—	—	—	—	—	74	
Moore	—	—	—	—	192·8	134	—	
Shukoff	—	—	—	—	—	—	—	—
Souchere	·15	0·9245	− 17 to 19	—	—	134-135	—	—
Stillwell	18	0·9245	—	—	—	—	—	—
Thorner	—	—	—	—	193-194	134 135	—	—
Ulzer	—	—	—	—	—	138·6	—	—
Valenta	—	—	—	—	194·6	—	—	—

TABLE SHOWING THE SPECIFIC GRAVITY, REFRACTIVE INDEX, IODINE VALUE OF FRENCH (OEILLETTE) AND INDIAN POPPY-SEED OIL. (ROYER.)

	Density at 15° C.	(Zeiss), Refraction at 25° C.	Iodine Value.	Bellier's Colour of the Acid.	Reaction Colour of the Oil.	Villavecchia and Fabris' Reagent.
1	0.924	72·0	132·9	Yellowish-white	Violet	Rose
2	0·9258	71·7	135·0	Green	Dark brown	Red
3	0.924	72·3	135·3	,,	Violet	,,
E	0·9243	72·6	136·1	,,	,,	,,
R	0·928	72·3	134·1	Pale green	,,	Rose
O	0·9257	72·6	137·2	Greenish-yellow	Brown	Salmon
P	0·9257	72·1	137·2	Yellow	Violet	Colourless
4	0·9239	72·3	132·1	,,	,,	,,
5	0·9242	72·0	136·7	Greenish-yellow	,,	Red
6	0·9249	72·7	137·8	Greenish-white	,,	Colourless
7	0·9245	72·8	138·5	Yellow	,,	,,
8	0·9240	72·5	136·8	Orange	,,	,,
A	0·9250	72·3	135·2	,,	,,	,,
B	0·9245	72·6	136·0	Greenish-yellow	,,	,,
C	0·9244	72·5	135·0	Pale green	,,	Rose
D	0·9243	72·3	134·9	,,	,,	,,
L	0·9240	72·4	136·3	,,	,,	,,
M	0·9260	71·2	129·8	?	?	Red
9	0·9239	72·4	135·8	Greenish-yellow	Violet	Rose
10	0·924	72·2	134·2	Pale green	,,	,,
11	0·924	72·4	135·5	Green	,,	,,
12	0·9241	71·4	134·9	,,	,,	Red
13	0·9242	72·5	135·6	Pale green	,,	,,
14	0·9245	71·5	133·5	—	—	,,

Samples Nos. 1 to 6 are Du Nord oeillette (1 cold pressed, 2 hot pressed, 3 hot pressed and refined). E, First pressure cold. K, Second pressure hot. O, Country pure Cassel. P, Ditto. 4, Cannes. 5, Marseilles. 6, Country oeillette seed. 7, Country oeillette, the two pressures mixed. 8, Country oeillette seed. B, Ditto. C, Exotic oeillette. D, Ditto. L, oeillette, first pressed Levant. M, Second pressed Levant. 9, Oeillette exotic, first pressed Indian. 10, Second pressed, ditto, Indian poppy.

Pumpkin-seed Oil.—The decorticated seeds of *Cucurbita pepo* yield by expression or extraction by solvents an oil—pumpkin-seed oil—which is extensively used as an edible oil (ranking next to olive oil); it is also used as an illuminant. The ether-extracted oil is used as a vermifuge. The cold-expressed oil is brownish-green and viscous, the extracted oil is redder. According to Poda expression in the cold is the general process of manufacture, but Graham states that most of the oil on the market is extracted by solvents, and that the expressed oil is more rare on the market and appreciably higher in price. Graham attributes to the different methods used to obtain the oil the variations in the chemical and physical properties of different samples of the oil. The oil is freely soluble in ether, carbon disulphide, and in twenty times its volume of absolute alcohol. It is endowed with appreciable drying properties

Exposed to the air for a time it forms a transparent yellowish mass. Its viscosity is high but not so high as olive oil. With the elaidin test it thickens slightly in 24 to 28 hours, becoming dark reddish-brown. Poda determined the index of refraction of fourteen samples of the oil. His readings varied from 70 to 72·5.

Senat Seeds.—A number of samples of the seeds of *Cucurbita Melo*, var. *agrestis*, were received from the Sudan. The forms of this plant represented in the present series included those known locally as "Senat," "Hameid," "Fagus," and "Tibish". The seeds yielded from 29·5 to 36·5 per cent. of a pale yellow liquid oil, which was free from smell and taste and would be suitable for edible purposes. These seeds are stated to be fairly abundant in the Sudan and a small export trade in them has already been developed.

Pumpkin seeds consist on the average of 76½ per cent. kernel and 23½ per cent. shell. The shell is yellowish, and the kernel is covered with a green skin. The whole seed gives on extraction about 37 per cent. of oil, the kernel alone about 48 per cent. In getting the oil by hot pressing about 10 per cent. of it remains in the press-cakes. The oil has a reddish-green colour and is very difficult to bleach. Sulphuric and sulphurous acids, as well as chlorine and ozone, had practically no effect upon the colour, which can, however, be reduced to a pale yellow by repeated treatment with caustic soda lye, although with considerable loss by saponification. The books give the percentage of oil at 20 to 25 per cent. only. The figures come, however, from Hungary, where the oil is extracted in a very wasteful and primitive manner.

Graham's estimate that the seeds of the pumpkin contain 25 per cent. of oil is inaccurate. Dr. Strauss obtained 37 per cent. from the whole seed, and 47 per cent. from the husked seed, by the extraction process. Pressure, of course, gives less. After one pressing at 80° to 90° C., 10 to 11 per cent. of the 37 per cent. remains in the cake. The oil has a deep reddish-green colour, and is very difficult to bleach. Caustic soda is the only substance that lessens the colour much, and it causes a good deal of loss by saponification. The oil extracted by ether gave an iodine number of 120·5, while that got by means of benzole or petroleum ether had an iodine number varying from 116·5 to 117·2.

Grimm (C.) gives the following constants: specific gravity at 15° C., 0·9286; solidification-point, - 8° to - 10° C.; refractive index at 15° C., 1·4805; acid value, 1·24; saponification value, 194·8; iodine value, 134·8; insoluble fatty acids, 94·8 per cent.

Robinia Oil (the so-called white acacia oil of the late Dr. Lewkowitsch, the *Weiss Akazienol* of the Germans) is not the product of an acacia tree at all but of the *Robinia pseudo acacia*, a plant belonging to the Jasmine family, but which the late Dr. Lewkowitsch confused with the yellow acacia, a true acacia, *Caragenia arborescens* belonging to the family of Legumenos, *q.v.* The author of this treatise

PUMPKIN-SEED OIL. TABLE OF CONSTANTS BY VARIOUS OBSERVERS.

Observer.	Specific Gravity.	Acid Value.	Saponification Value.	Iodine Value.	Solidification-point.	Hehner No.	Melting-point of Fatty Acids.	Solidification-point of Fatty Acids.
Henriques . . .	—	—	—	121·5	—	—	—	—
Hübl . . .	—	—	—	121	—	—	—	—
Graham . . .	0·9208	18·9	192·5	—	—	—	—	—
,, . . .	0·9197	3·5	195·2	—	—	—	—	—
Poda . . .	—	—	189·3-189·5	124·5	—	—	—	—
,, . . .	—	—	189·3-189·4	123·7	—	—	—	—
,, . . .	—	—	189·9	125·1	—	—	—	—
,, . . .	—	—	189·6	124·3	—	—	—	—
,, . . .	0·923-0·925	—	188·4-190·2	122·76-130·7	—	—	26·5-28·5 28·4-29·84	—
Schadler . . .	0·9231	—	188·1	—	15° C.	—	28° C.	—
Schœtenfrier . .	0·9230	—	188·7	113·4	− 16° C.	96·2	—	24·5

cannot understand how palpable bungles like these can be perpetuated in a twentieth-century work published in England, seeing that the *Robinia* has been an ornamental tree grown in the demesnes of noblemen and gentlemen in England for a couple of centuries at least. A very excellent monograph on the *Robinia* of over 400 pages was compiled as far back as about 1820, from which it appears that the *Robinia* affords an excellent timber. It is most reprehensible that those interested in drying oils should have the false idea conveyed to them that this so-called white acacia, whose distribution is world-wide, should have its habitat so erroneously confined to South Russia.

Wild Safflower-seed Oil.—From this title it will be at once seen that there is a cultivated variety of safflower, the seed of which also yields oil, but that oil is described separately (pp. 451-453). Wild safflower-seed is the product of the *Carthamus oxycantha*, a native of arid tracts of land in North India. Let it be well understood that it has nothing to do with saffron (*Crocus Sativus*). It is especially abundant in Peshawar, where the spinose clumps are an objectionable feature of the grassy tracts. Where the plant is fairly abundant the seeds (fruits) are collected for their oil, which is the chief ingredient in Afridi waxcloth. Crossley and Le Soeur examined a sample of this oil, $D\frac{15{\cdot}5^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}} = 0{\cdot}927$; acid value, 3·66; Hehner value, 95·44; saponification value, 189·4; iodine value, 135·49; refractive index at 40° C., 68·2. Wild safflower-seed oil is extracted from the *Carthamus oxycantha* by a cold process. It is then run into earthen vessels and "boiled" continuously for 12 hours. The vessels in which the oil is boiled are so fixed that a flame cannot reach the boiling oil, and the temperature is kept low and well regulated so as to maintain a uniform heat. After a certain time it begins to emit volumes of white pungent vapour, so that wild safflower oil boilers have to conduct their business under a special licence far remote from human habitations. When the oil has been "boiled" to a sufficient extent the still hot oil is run into large shallow trays containing water; it swells up into a jelly-like substance, the roghan of North India, which is packed in tin cans for despatch to the manufacturers of Afridi waxcloth.

The Manufacture of Afridi Waxcloth.—In this industry the paint is not applied by a brush but by an iron style. The deftness, rapidity, and accuracy with which the pattern is elaborated from threads of plastic-coloured roghan must be seen to be appreciated. The skilled craftsman works from left to right or right to left with equal ease and freedom, and, as in handwriting, the thick down strokes and the fine hair up strokes each keep their own place in the elaboration of the pattern covering the fabric. When two or more colours are given the craftsman generally applies all the patches or lines of one colour before the second or third. The half-finished table-cloth or fire-screen may thus appear bewildering, as it may be impossible to discover the actual pattern in the mind of the craftsman. In Baroda castor oil, and in Kach linseed oil are used to make the roghan used in the manufacture of oilcloth in these localities. Tests made in the Calcutta Industrial Museum showed that wild safflower oil possesses no special advantages over the oil from the cultivated safflower. India exports the jute textiles used in the linoleum, and Sir George

Watt urges the importance of India making her own waterproofs, linoleum, and waxcloth, and ceasing to pay tribute to the waxcloth and linoleum manufacturers of Europe, who now supply India with the bulk of these products made with raw materials imported from India.

Cultivated Safflower-seed Oil.[1]—This oil is derived from the seeds of the cultivated safflower *Carthamus tinctoria*, a plant which is cultivated, more or less, all over India, sometimes for dyeing purposes, sometimes for oil producing. Many points as regards its cultivation are highly interesting, but to enter the domain of Indian agriculture would carry us too far. So also all reference to the use of certain parts of the plant for dyeing purposes and for the manufacture of lakes must be rigidly excluded. The seed is very small, 100 of them only weighing ⅛ to ¼ oz., and it is covered with a thick husk. The seeds from the dye-yielding plant are collected and form an additional income. However, in some provinces, especially Bombay, an oil-seed crop is specially grown. "Safflower," according to Mollison, "is the most important oil-seed crop in the Bombay Presidency. The area is usually from 500,000 to 600,000 acres annually. The chief centres of cultivation are in the black rabi lands of Ahmednagar, Poona, Satara, Bijápur Dharwar, and Belgaum. It is subordinate to the crops with which it is associated, such as jiur, wheat, or grain. It therefore participates in the general cultivation given to these crops. Usually, three consecutive rows of safflower alternate with 9, 15, or 21 of the principal crop." In the Central Provinces the area of special oil cultivation has recently been greatly curtailed, so that the Deccan production may be accepted as alone of importance, though the oil of the dye crop must not be entirely ignored. Not only are there two distinct sources of the oil, but there are also two quite different methods of extraction. (1) The seeds are cold pressed, either before or after being decorticated. The yield is said to average 20 to 30 per cent., but both the quality of the oil and the value of the cake depend on the seed being decorticated. The cold-drawn oil has a clear straw-yellow colour of specific gravity 0·9224 at 15° C.

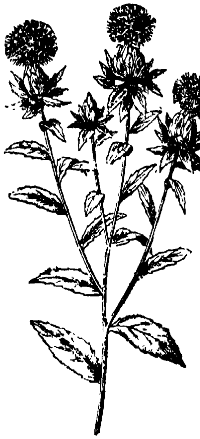

FIG. 109.—*Carthamus tinctoria.* The source of safflower-seed oil.

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[1] Lewkowitsch gives saffron oil as a synonym for this oil, a most misleading thing to do. True safflower is occasionally termed *bastard saffron*, but that misleads no one.

It possesses pronounced drying properties, readily saponifies with alkalies forming a fairly good soap, and the free fatty acids have some of the characteristics of the linoleic acid obtained from linseed. The oilcake retains 11·55 per cent. of the natural oil, and is not contaminated with earthy impurity. The nitrogen amounts to 3·19 per cent. which is equivalent to 19·94 per cent. of albumenoids. It is an oil extensively used for culinary purposes, and to adulterate *ghi* or *til*. Moreover, safflower earth-nut and till are mixed, and the different seeds so mixed together crushed. The oil which exudes from this mixture forms the sweet oil of Bombay. Inferior grades of cold-crushed oil are used for illumination.

Hot Expressed Safflower-seed Oil.—The second method of extracting safflower-seed oil is a hot dry extraction, or rather a crude downward distillation. The seeds are placed within an earthen pot and this is inverted over the mouth of a similar pot placed within the ground, the two pots being separated by a perforated plate. Over and above the inverted pot is piled some fuel, and on this being ignited the seeds are partly roasted. The oil in consequence drains from them, and accumulates in the lower or submerged pot. The yield of oil in the hot extraction process is about 25 per cent. (greater than in the cold), but is useless both for burning purposes and for food. It has, in fact, acquired a new property, being converted into a substance, very serviceable for greasing well ropes, leather well buckets, purposes for which the cold-drawn oil is quite unsuited. In other words, the oil has been converted into what is known as roghan, a substance used to prevent leather from hardening on its being exposed to the action of water, or of a damp atmosphere. The oil would appear to be converted into an analogue of sod oil, the so-called *degras*.

SAFFLOWER-SEED OIL. TABLE OF CONSTANTS.

	Temperature.	Density.	Hehner Value.	Saponification Value.	Reichert-Meiszl Value.	Iodine Value.	Refractive Index.
Andés . .	15° C.	0·9246-0·928	95·4	186·6-194	—	127·9-149·9	1·477 at 16° C.
Crossley and Le Soeur . .	$\frac{15}{15}\frac{5}{5}$° C.	0·9251-0·928	95·3	186·6-192·5	—	129·8-149·9	65·2 Zeiss, Butyro refractometer at 40° C.
Jones . .	20° C.	0·9227	—	194-194·8	—	143-144·5	
Shukoff . .	—	—	—	195·4	—	141·6	
Tylaikold . .	0° C.	0·934-6	—	172 (?)-194	0·69-0·88	126-130	
,, . .	15·5°C.	0·916-0·925	—	—	—	—	

The insoluble fatty acids according to Andés amounted to 95·4 per cent. with the following constants:—

CONSTANTS OF FATTY ACIDS OF SAFFLOWER-SEED OIL.

Specific gravity at 16° C.	0·9315
Melting-point	16° C. to 16·5° C.
Neutralisation value	199
Iodine value	132·5 to 148·2

Oil of Soja Hispida (*Soja Bean*).—The *Soja Hispida* is a herbaceous plant of the *Leguminoseæ*, indigenous to China and Japan, where the seeds are highly valued as an edible food. The seeds contain a large quantity of fermentable sugar, also a ferment similar in its properties to diastase; the oil, present in the proportion of 14 to 18 per cent., can be extracted by pressure or by means of ether; it possesses laxative properties, a yellowish-brown colour, and a slight aromatic odour. It readily solidifies, and is intermediate between the drying and non-drying oils. The following properties are given, which are confirmatory of those obtained by Stingl and Morawski (*Chem. Zeit.*, 1886, 140):—

Specific gravity at 15°	0·924
Point of solidification fatty acids	8° to 15°
,, ,, fusion	27° to 29°
,, ,, solidification	23° to 25°
Temperature rise	59°
Iodine number	121·3
,, ,, of fatty acids	122
Saponification number	192·5

The oil gives with Hauchecorne's reagent a dirty white coloration in the cold, but deep orange when heated; with Brulle's reagent a deep orange, but no coloration with Bechi's reagent.

Chinese Bean Oil.—The technical literature of the early years of the present decade, when linseed oil was nearly as dear as during the present war, was flooded with all sorts of extravagant assertions as to the value of the Chinese bean oil as a drying oil. Some of these absurd notions—they cannot be regarded as serious propositions—did not stop short at recommending Chinese bean oil as a substitute for linseed oil. The former was alleged by men of "light and leading" to be a far superior drying oil to the latter, and this technical untruth was followed up by a propaganda, the object of which was ostensibly to depreciate the long-established good qualities and virtues of linseed oil as a drying oil, and to magnify in the most grotesque manner possible those of the Chinese bean oil. Linseed oil as a drying oil did not have a single good point! Although oiled silk and oilskin garments had been worn long beyond the memory of man, a linseed oil film was not waterproof; and if fishing-net buoys had for years borne the heavy deadweight of fishing nets loaded with tackle weighing many tons, and a catch of fish often weighing tons if not hundreds of tons without additional submersion, thus proving that linseed oil not only gives a waterproof, but an airproof film when made into paint—all that counted as nothing.

Chinese bean oil cannot be in any sense of the word a drying oil. Nevertheless the iodine values of Chinese bean oil flatly contradict its responding to the elaidin test, which is too often performed in the most slip-shod manner conceivable.

Bean Oil, Chinese Mode of Preparation.—According to Korentcheff and Zimmernlen, an analyst and pharmacist attached to a Russian hospital during the Russo-Chinese war, the first process consists in crushing the beans into cake or a mass with the destruction of their skins. A large grindstone lies upon the ground, and upon it another but smaller grindstone turns on its axis, the motive power being the usual ox traction. In front of the smaller stone an apparatus is fitted holding a basket, out of which the beans are poured under the small millstone. And behind the same millstone another apparatus is fixed which directs the beans pressed by it into the centre of the larger millstone.

In the second process the beans that have been crushed are heated in cloths over a stone plate until they begin to steam. The heated bean cake is then gathered on to iron discs, over which it is subjected to a very heavy pressure. The expressed oil flows into circular grooves that go round the frame of the press, whence it passes into vessels prepared for it.

Without further manipulation the oil so expressed is often sold from the factories. Just, however, after it has been expressed it has a cloudy appearance. But, if allowed to stand, the impurity will settle, and a sediment will form at the bottom, leaving a fine clear

TABLE SHOWING THE CHEMICAL AND PHYSICAL CONSTANTS OF FOUR DIFFERENT SAMPLES OF CHINESE BEAN OIL.

	Samples.			
	1	2	3	4
1. Colour	All dark brown			
2. Consistency	All fluid			
3. Smell, growing stronger with heating, resembles wood oil .	Insignificantly	Notably	Slightly	Slightly
4. Taste recalls that of other vegetable oils . . .	—	—	—	—
5. Solubility in ether	All complete			
6. Water content.	1·80 %	0·59 %	0·34 %	0·13 %
7. Specific gravity at 15° Cel. .	0·9264	0·9237	0·9270	0·9276
8. Solidifying-point	– 15°	– 14·8°	– 15·3°	– 14·6°
9. Saponification value . .	207·9	211·6	208·0	209·8
10. Ether value	206·8	203·9	206·8	207·7
11. Iodine ,, (Hübl). . . .	114·8	126	137·2	130·17
12. Fatty acid	94·28 %	94·02 %	93·88 %	93·60 %
13. Solidifying-point of fatty acids	+ 16·4°	+ 16°	+ 17°	+ 17·3°
14. Melting-point ,, ,,	+ 20·5°	+ 20°	+ 21°	+ 21°
15. Maumene test	104°	120°	116°	104°
16. Elaidin reaction	All positive			
17. Animal oil 18. Mineral ,, 19. Metal	No trace			
20. Acid value	1·86	15·46	3·92	3·76

oil. When this sediment is subjected to the microscope it is seen to consist principally of bean refuse and a small proportion of sand.

In a paper read by H. A. Gardner before the Canadian Association of Master Painters, he describes a whole series of experiments which he made to accelerate the drying of soya bean oil. This paper deals with the question so fully and exhaustively that it is given here as reproduced by the "Oil and Colour Trades Journal":—

"*Driers for Soya Bean Oil.*—If soya oil has been classed as a semi-drying oil, having an iodine value of approximately 130, it is a far better drying oil than other oils of similar iodine value. It is especially adapted for use in the manufacture of paint, treatment with a small quantity of drier serving to set it up in a short time to a firm, elastic film. The type of drier to use with soya oil, however, is a matter of great importance. In the same way that lead, zinc, lithopone, and other pigments give better results with different kinds of drier, various oils are also affected through the use of driers of different types. In a recent lecture, Toch proposed for soya oil the use of driers made from the metal cobalt. In order to determine the relative effect of cobalt driers as compared with the more commonly used lead manganese driers, Gardner made a series of experiments upon a laboratory scale. Before the results are accepted commercially the tests should be repeated upon a larger scale. A series of eleven soya oils as obtained in the market, and representative of the grade of oil that was then being furnished by the grinders, were treated separately with nine different driers. The driers were carefully prepared for the test, each containing approximately the same metallic content.

"*Description of Driers.*—No. 1. Cobalt linoleate in turpentine and benzol (contains 6 per cent. cobalt oxide). No. 2. Cobalt rosinate in turpentine and benzol (contains approximately 6 per cent. cobalt oxide). No. 3. Lead tungate in turpentine and benzol (contains approximately 5 per cent. litharge. No. 4. Lead and manganese rosinate (contains approximately 4 per cent. litharge and 2 per cent. black oxide of manganese). No. 5. Manganese rosinate in turpentine and benzol (contains approximately 6 per cent. black oxide of manganese). No. 6. Lead tungo-rosinate. No. 7. Lead linoleate (contains approximately 6 per cent. litharge). No. 8. Cobalt and lead linoleate (contains approximately 4 per cent. cobalt oxide and 2 per cent. litharge). No. 9. Cobalt and lead rosinate (contains approximately 4 per cent. cobaltic oxide and 2 per cent. litharge). In making the drying tests, 10 parts of oil were placed upon a glass plate. There was added to the oil 1 part of the drier, and after a thorough mixing with a clean camel's hair brush, the oil was uniformly spread over the surface of the plate, cross-brushed and set aside to dry. The temperature of the laboratory was approximately 70° F. and the humidity was high. The painted plates were examined every 8 hours to determine whether any marked drying had taken place. At the end of a 24-hour test, the various driers gave the following results on the eleven samples of oil which were under test:—

No. 1 drier gave fair results on 10 samples of oil.
,, 2 ,, ,, ,, 9 ,, ,,
,, 3 ,, ,, ,, 6 ,, ,,
,, 4 ,, ,, ,, 3 ,, ,,
,, 5 ,, ,, ,, 6 ,, ,,
,, 6 ,, ,, ,, 2 ,, ,,
,, 7 ,, ,, ,, 7 ,, ,,
,, 8 ,, ,, ,, 11 ,, ,,

"From a consideration of the results, it is shown that of the common driers, lead linoleate is probably the most efficient. Of the newer driers, however, those containing cobalt seem to have given the best results. It occurred to the writer that a drier made by combining lead and cobalt might be still more effective. This seems to be true from the results obtained with Nos. 8 and 9. No. 9 was adopted as a working drier in some further tests which were carried on, and which are described below.

"There was obtained through the courtesy of Mr. C. Piper, Agrotologist in the Bureau of Plant Industry, United States Department of Agriculture, a series of twenty-four samples of soya bean oil crushed from seed grown at the Arlington Experimental Farm of the Department, where the culture of soya beans has been studied for some years. These oils were tested along the same lines as outlined above, drier No. 9 being used throughout the test. The oils were examined for their iodine value and the results of the tests are charted as follows:—

Oil No.	Variety.	Seed Colour.	Iodine No.	Drying of Oil in 8 Days.	Drying in 24 Hours with 5 per Cent. Drier No. 8.
16789	Flava . . .	Straw-yellow	131·3	Poor	Good
16790	Cloud . . .	Black	133·7	,,	,,
17252	Flat kind . .	,,	130·2	Good	,,
17252C	Field . . .	,,	133·8	,,	,,
17253	Nuttall . .	,,	129·8	,,	,,
17254	Ebony . .	,,	132·1	,,	,,
17263	Austin . .	Olive-yellow	131·2	,,	,,
17264	Tokio . . .	,,	133·4	,,	,,
17267	Hope . . .	,,	123·5	,,	,,
17268	Ito San . .	Straw-yellow	132·8	,,	,,
17271	Haberlandt .	,,	134·1	,,	,,
17278	Hollybrook .	,,	135·0	,,	,,
17852	Meyer . .	Black and brown	137·4	Poor	,,
17852B	Peking . .	Black	131·4	,,	,,
17861	Jet . . .	,,	130·8	,,	,,
18227	Chernic . .	,,	134·8	,,	,,
18259	Pirgsee . .	,,	134·5	Good	,,
19163	Wilson . .	,,	125·1	Poor	,,
19186	Morse. . .	Olive-yellow	131·0	,,	,,
21079	Shingto . .	,,	129·9	,,	,,
21079B	Auburn . .	Black	123·7	,,	,,
21999	Taha . . .	Black and Olive	129·9	Good	,,
22312	Farnham . .	Straw-yellow	127·8	,,	,,
23232	Klangau . .	Dull brown	133·9	,,	,,
25000	Mammoth . .	—	132·4	Poor	,,

"It is shown above that although the various samples of oil tested differed in their drying values, they all become dry when treated with an efficient drier."

Oil from the Seeds of Fir Trees.—Rohdich has investigated the possibility of obtaining oils from the seeds of fir trees. No difficulties arise in the treatment of fir seeds. Experiments on a small scale have shown that the seeds of the conifers, when ground and extracted with ether, yield 20·85 to 31·20 per cent. of oil. These figures show that the trees in question can form a valuable source of oil, more especially since they do not have first to be planted, but already exist in large numbers and yield a crop every year. The labour of collecting the fruit and seeds need not be expensive. In addition to

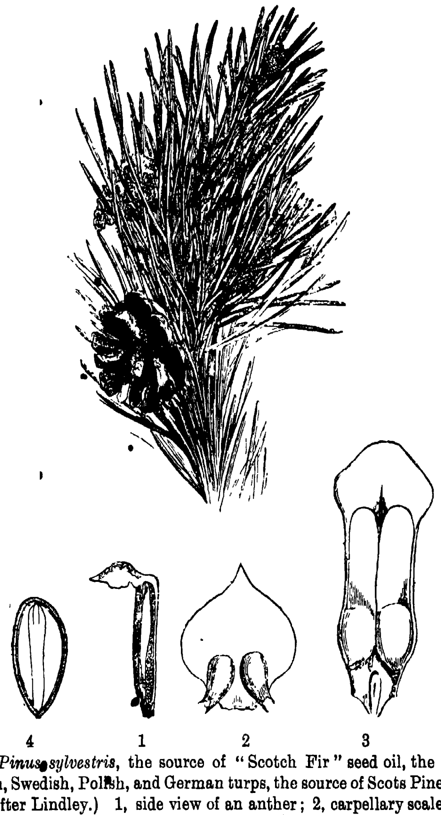

FIG. 110.—*Pinus sylvestris*, the source of "Scotch Fir" seed oil, the source of Russian, Swedish, Polish, and German turps, the source of Scots Pine essential oil. (After Lindley.) 1, side view of an anther; 2, carpellary scale and pair of inverted ovules; 3, inside of ripe scale and seeds; 4, section of the seed, minus the wing at its base.

oil, the seeds contain 35·2 to 35·3 per cent. of nitrogenous substances in the case of the conifers, so that the press-cakes could form a valuable cattle food; the seeds themselves are readily eaten by the wild animals inhabiting the woods.

But it is not enough that the yield of oil per cent. should be considerable but that the crop of cones yielded by the pines should also be considerable, and that a sufficient number of pine forests should be available for cone picking, and that the crop should be far in excess of that required for nursery purposes. At present the yield is so small that it is quite insufficient for planting purposes so as eventually to maintain the pine forests in pre-war head of standing timber. *N.B.*—The cone is about a cubic inch, but the yield of seed per cone occupies only a few $\frac{1}{100}$ths of an inch.

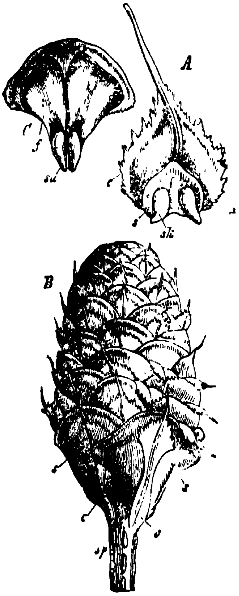

FIG. 111.—*Abies pectinata.* The silver fir.
A, bract; *c*, detached from the axis of a young cone, with the scale; *s*, bearing the ovules, *sk* (magnified). *B*, upper part of mature cone; *sp*, axis; *c*, bracts; *s*, largely developed scales, bearing the seeds on the upper surface (reduced). *C*, ripe scale, with two winged seeds; *sa*, seed; *f*, wing (reduced). (After Schacht).

Scots Pine Seed Oil.—The author having complained to the Director of the Botanic Gardens, Kew, about certain points in an article in the "Kew Bulletin," Nov. 6, 1915, on the subject of the Scots Pine, was favoured with the following memorandum in reply:—

"*Subject.*—Scots Pine in 'Kew Bulletin,' Nov. 6, 1915.

"The name of Scots Pine is applied generally to *Pinus sylvestris* in the British Isles, whether the trees have been raised from home-grown or continental seed. Some nurserymen, however, indicate the source from which their seed has been obtained. It is more than likely that distinct races of *Pinus sylvestris* exist, but whether the distinctive characters are sufficient to warrant separate varietal names except in two or three instances, is very doubtful. When seeds are collected from trees growing under very different conditions and sown side by side, the seedlings from different regions show considerable variation in rate of growth, but botanically all are *P. sylvestris*. The height of the Scots Pine is given as up to 140 to 150 feet, not the average height. The height given is reached under the most favourable conditions in some of the continental forests. In Scotland the tallest trees noted are between 95 to 111 feet high, but the average height for well-grown examples is probably nearer 75 to 80 feet."

Stillingia Oil.—The oil known as stillingia oil is, according to Watt, obtained from the seeds of *Tapium Sebiferum*, which is the same tree as that which yields Chinese tallow. The Chinese tallow tree is a small glabrous tree, indigenous to and cultivated in China and Japan, introduced into and cultivated in Northern India, having become almost wild in the Dun, fairly abundant in Garwhal, Kumaon, and Kangra. The plant is easily raised from seed, but is usually propagated by layers or cuttings. The fruit is a 3-cell capsule, each cell with a single seed surrounded by a thick greasy substance, the so-called vegetable "tallow". In addition to this solid fat, the seed kernel yields about 50 per cent. of a brownish-yellow oil, which is employed medicinally, also as a burning oil, and in the preparation of umbrella varnish. The oil is obtained by expressing the seeds after steaming them to liberate the tallow. The oil is limpid and of a pale yellow colour; it has a peculiar smell similar to that of linseed oil and mustard oil. It can be distinguished from linseed oil by its great levo-rotary power.

STILLINGIA OIL. CHEMICAL AND PHYSICAL DATA.

Observer.	° C.	Density.	Saponification No.	Iodine No.	Refractometer No.	Hehner No.	Thermal Test, Maumené.	Refraction.
Hobein .	15	0·9458	203·8	145·6	—	—	—	Butyro refracto degrees 75 at 35° C. Index of refraction at 25·5, 1·4825
Nash .	15·5	0·9395	—	160·7	—	—	—	
Tortelli &Ruggeri	27	0·9432	210·4	160·6	0·93	94·4	136·5	
	15	0·9370	—	—	—	—	Specific temp. reaction, 267	
	15	0·937	—	—	—	—		

STILLINGIA OIL. FATTY ACIDS.

Observer.	Solidification-point.	Melting-point.	Neutralisation No.	Iodine No.
Lewkowitsch . .	—	—	206·3 Saponification No. 210·5	Liquid 191·1 „ 181·8
Nash . . .	—	—	—	165
Tortelli and Ruggeri . .	12·2	14·5	214·2	Liquid 161·9 „ 178·1

More recently it has been found that the most characteristic property of stillingia oil is its optical activity. It rotates the plane of polarised light strongly to the left, viz. – 6° 45′ in a 200-millimetre tube, corresponding to – 29·9 saccharimetric degrees. As croton oil is derived from *Croton Tiglium* and stillingia oil from *Croton Sebiferum* its optical activity can very well be understood. But whereas croton oil deviates to the right, stillingia oil deviates to the left. In general, oils and fats only exert a feeble action on polarised light. However, some distinguish themselves from others by being more active, a property which may be used to identify them or to enable them to be recognised in admixture. When the deviation is feeble it may be ascribed to cholesterin or phytosterin, according to whether it is a question of an animal or vegetable oil. But where there is a strong deviation with a pure oil it is undoubtedly due to the action of the glycerides themselves. Cholesterin and phytosterin being lævo-rotary impart to oils the property of deviating the plane of polarisation to the left.

Sunflower Oil (English, Sunflower Oil; German, Sonnenblumeöl; French, Huile de tournesol).—The sunflower, a native of Mexico, is a plant of the Composite Order, the botanical name of which is *Helianthus Annuus*, L. The sunflower has long been cultivated in Europe as an ornamental plant. It is grown on a large scale in Hungary and Russia, more especially in the Russian Province of Kuban, where the plant is not only cultivated for its oil but as a source of potash. The seed kernels are crushed in Russia for oil, and are also exported for crushing in other countries. Germany, prior to the war, did a considerable trade with Russia in sunflower oil. The kernels contain about 50 per cent. of oil. The yield of oil calculated to the seed is about 20 per cent. The cold-pressed oil is a pale yellow oil with a pleasant smell and mild taste, which is used as an edible oil. The second hot-pressed oil yields a dark oil, which is used as an illuminant and for soap purposes, also as a paint vehicle and as boiled oil. The saturated fatty acid content is very small, only about 3·9 per cent. according to Vorleker, and here the similar data of Hazura comes into play. Hazura found 92·5 per cent. of fluid fatty acids which yield on oxidation dioxystearic acid and sativic acid behaving like oleic and linolic acids. If 130 be taken as the mean iodine number it would about correspond with the calculated iodine number of equal weights of oleic and linoleic acid. The iodine number of sunflower-seed oil at first sight indicates only a slow drying oil. Hübl by treating it with copper powder found it to dry in 7 days with an oxygen absorption of 5 per cent., but J. Petroff obtained unsatisfactory results with sunflower oil as a raw material for boiled oil. The following are his results:—

TABLE SHOWING THE COMPARATIVE TIME OCCUPIED IN DRYING OF RAW AND BOILED SAMPLES OF SUNFLOWER SEED OIL.

	Time of Drying.
Raw sunflower seed oil	8 days
,, ,, ,, heated and blown for 4 hours at 200 to 250° F. . . .	8 ,,
Raw oil, with 2 per cent. of MnR	15 hours
,, ,, 2 ,, of MnL	38 ,,
Blown oil, ,, 2 ,, of MnR	25 ,,
,, ,, 2 ,, of MnL	38 ,,

Twenty-five parts of the boiled oil mixed with 20 parts of white lead or zinc white took 30 hours to dry, the usual time being 8 to 9 hours. Sunflower-seed oil as a raw material for oil boiling is undesirable (Petroff). But according to Bock, who has resided in Russia, much sunflower-seed oil is used there in paint-grinding, whilst the greater part is used as an edible oil, the seed being heated before expression to develop a peculiar aroma; the oil for varnish is prepared by steaming the seed and treating the expressed oil with fuller's-earth so as to eliminate the mucilage which causes foots. If the manufacturer does not crush the seed himself he must make preliminary tests to see if the oil is fit for varnish-making. A pale oil for varnish-making is obtained by treating the oil with 1 per cent. of fuller's-earth and heated to 300° C. until it thickens, without browning; this oil is mixed with equal parts of hardened rosin, a pale drier is added, and the product ground with white zinc. The paint so obtained is characterised by its brilliant white and its permanence to atmospheric agents without any tendency to yellowing. The same oil may be used with copal and its analogues.

PHYSICO-CHEMICAL CONSTANTS OF MIXED FATTY ACIDS FROM SUNFLOWER-SEED OIL.

	Melting-point.	Solidification-point.	Saponification Value.	Iodine Value.
Bach	23° C.	17° C.	—	—
De Negri and Fabris	22-24° C.	18° C.	—	—
Dieterich . . .	23° C.	18° C.	—	—
Jean	22° C.	—	—	—
Peters . . .	17-22° C.	—	—	—
Spuller . . .	—	—	201·5	133·2-134
Thorner . . .	23° C.	17° C.	201·6	133-134

PHYSICO-CHEMICAL CONSTANTS OF SUNFLOWER-SEED OIL.

Observer.	Specific Gravity.	Solidification-point.	Hehner Value.	Saponification Value.	Iodine Value.	Maumené Test.	Refractive Index.
Allen	0·924-0·926	—	—	—	—	—	—
Beckarto and Seiler	—	—	—	—	—	—	72·2 at 25° Zeiss
Bornemann	—	− 16 to − 18·5	—	193-194	—	—	—
Chateau	0·924-0·926	—	—	—	—	—	—
De Negri and Fabris	0·926	—	—	188-189	119·7-120·2	72-75° C.	—
Dieterich	0·936	—	—	—	122·5-133·3	—	—
Holde	0·9240	Still solid at − 17° C.	—	193	135	—	—
Jean	0·9250	—	—	192	124	—	+ 35°
Spuller	0·9258	—	95	193-193·3	129	67·5° C.	1·4611 at 60° C.
Thorner	—	—	—	193-194	129	—	—
Holde	0·919 at 40° C.	—	—	—	—	—	—

Tobacco-seed Oil.—According to Cohen about 3 cwt. of tobacco seed is obtained from an acre of tobacco. This 3 cwt. of seed yields 1¼ cwt. of oil or 41·6 per cent. The seed should be harvested after the top leaves have been collected. There are difficulties encountered

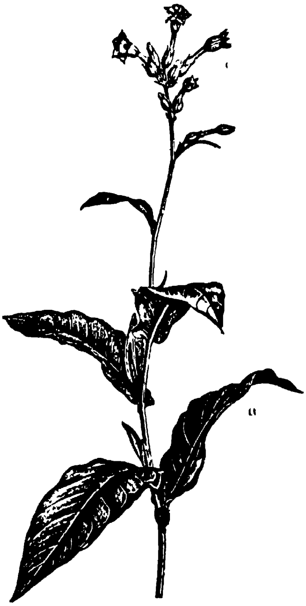

FIG. 112.—*Nicotiana Tabacum*, the tobacco plant (source of tobacco-seed oil).

in the collection of the seed and in the drying of it. The oilcake contains 4·2 per cent. nitrogen.

Walnut Oil.—Oil of walnut can readily be extracted by pressure from not over-ripe nuts, as also from the kernels by ether or carbon disulphide; it is of a yellowish colour, and is used in some countries, especially Piedmont, as a good substitute for olive oil. The following data are given:—

Specific gravity at 15° C.	0·9265
Melting-point of fatty acids	16° to 18°
Temperature rise	96°
Iodine number	144·5 to 145·1
,, ,, of fatty acids	150·05
Saponification number	193·8 to 197·3

Its specific gravity, rise of temperature, and high iodine number distinguish it from other oils obtained from nuts. It gives a brown coloration with Heydenreich's, reddish-brown with Hauchecorne's, and an intense orange coloration with Brulle's reagent.

Walnut Oil. The Arboriculture and Horticulture of the Walnut Tree.—The common walnut tree is a native of Persia. It has been utilised and cultivated in India since very remote times. It is conjectured to have been introduced from France into England in or prior to 1562. The tree was highly esteemed by the Romans; hence the generic name *Juglans* or *Jovis glans* or Jove's nut acorn, the specific name *regia*, the queen, from its pre-eminence among nuts. Walnut, its common name, is said to be derived from Gaul nut, the nut of Gaul, from whence it came.

Synonyms:—

British—Walnut.
French—Noyer.
Dutch—Walnoot and Ockernoot boom.
German—Walnussbaum.
Italian—Noce.
Spanish—Nogal.

However important the oil may be, the chief value of the tree lies in its timber, the most important use of which is for gun-stocks, and as the European supply is nearly exhausted, the more extended cultivation of the tree in India is suggested. But the *vis inertia* of the Indian forestry official is proverbial. The walnut, which ripens in India in July to September, is an important article of diet in Kashmir and the N.W. Himalayas generally, and is largely transported to the plains. Both the leaves and the oil have been largely employed in destroying intestinal worms. "The more walnuts one eats, the more ease will he drive worms out of the stomach" (Pliny). Green walnuts make an excellent pickle, and for this purpose should be gathered before the stone becomes so hard as to be felt when pricked with a needle.

Soils in which to Plant Walnut Trees.—In good soils the tree will thrive for a century and bear nuts to the last. The tree begins to bear when about 20 years old. In some light soils, and probably when the roots have been confined, walnut trees have been known to bear nuts when under 10 years, but by the process known as budding, Knight has shown that they will fruit in 3 or 4 years. The fruit should be allowed to ripen on the tree, and to fall of its own accord, when the nuts may be gathered, deprived of their husks, dried, and preserved in sand till wanted for use.

Propagation of the Walnut Tree.—The tree is propagated for general purposes by seed sown in spring in nursery beds or broad drills, being transplanted the following autumn, but more generally the second autumn. The strongest plants might be drawn out the first autumn for transplanting, leaving the smaller, which then would have plenty of room, to the next planting season. This is the most eligible way when the trees are required for timber, but for fruit, the best varieties, of which there are several, should be taken from the fruit-bearing trees, and inarched or budded on young healthy seedling stock. This latter method of propagation was suggested by Boulcher, an Edinburgh nurseryman, about the beginning of the 18th century. Abercrombie practised it. The late Mr. Knight about 1814 suggested the practice of budding. The walnut formed an exception to the usual method of inserting the buds in shoots, of the same years possibly in some measure, because its buds contain within themselves in the spring all the leaves which the tree bears the following summer, whence its annual shoots wholly cease to elongate soon after its buds enfold. All its buds for each season are also consequently very nearly of the same age, and long before any have acquired the proper degree of maturity for being removed, the annual branches have ceased to grow or to produce new foliage. Knight pointed out that there are at the base of the annual shoots of the walnut and other trees, where those join the year old wood, many minute buds which are almost concealed in the bark and which rarely or never vegetate except in the event of the destruction of the large prominent buds which occupy the middle and opposite ends of the annual wood. By inserting in each stock one of these minute buds and one of the large and prominent kind, Mr. Knight found that the minute buds took freely, whilst the large all failed without a single exception. This experiment was repeated upon two-yearling stocks which grew in pots and had been placed during spring and the early part of summer in a shady situation under a north wall (Mr. Knight's method of retarding vegetation), whence they were removed late in July to a forcing-house and instantly budded. These being suffered to remain in the house during the following summer produced from the small buds shoots nearly 3 feet long, terminating in large and perfect female blossoms which necessarily proved abortive as no male blossoms were procurable at the early period in which the female blossoms appeared, but the early formation of such blossoms sufficiently proves that the habits of a bearing branch of a walnut tree may be transferred to a young tree by budding as well as by engrafting by approach. The most eligible spot for the insertion of the buds of this species of tree and possibly of others of similar habits is near the summit of the wood of the preceding year, and, of course, very near the base of the annual shoot, and if buds of the kind above mentioned be skilfully inserted in such part of the branches of rapid growth, they will be found to succeed with nearly as much certainty as those of other fruit trees provided such buds be in a more mature state than those of the stock into which they are inserted. Layers make inferior plants and grafting is not very successful, but marching may be readily performed during February or March. Budding is, however, by far the best method, for it would often be found impossible to march shoots of a superior kind, the branches of which might be 20 feet from the ground upon a stock of 6 or 8 feet in height.

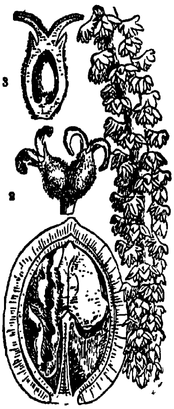

FIG. 113.—*Juglans regia;* 1, a ♂ catkin; 2, a pair of ♀ flowers; 3, perpendicular section of a ♀ flower; 4, perpendicular section of a ripe walnut. (After Lindley.)

The Best Varieties of Walnut.—The fruit of the walnut being of much importance in climates suitable to their ripening, and as there are so many superior sorts to be met with, it would be well if nurserymen would bestow more attention to the matter. The best varieties of walnuts are the large double-kerneled French, the tender or thin shelled, a very fine variety, both of which are grown about the village of Worthy, near Winchester, the Highflyer of Thetford, and the new Divant Prolific or Noyer fertile, raised from seed at Chalons. Mr. Rivers says he saw plants of this sort in Paris only 2 feet in height and full of fruit. Mrs. Harvey, "Adventures of a Lady in Tartary," speaks of a walnut cultivated in the Valley of Kashmir with a shell as thin as paper and easily broken by the hand. The Highflyer of Thetford has a shell nearly as thin, and is on that account a variety deserving of more general cultivation.

Soil and Situation.—The walnut will succeed in any ordinary soil if on a dry sub-soil, and the best situation is in a warm sheltered part of the demesne where they will become both ornamental and useful. They are rather large for garden culture unless attention be paid to root and branch pruning. One objection to them in gardens is the space they would occupy and the shade they would produce.

Disease and Insects.—The walnut is proverbially exempt from these. Its leaves are used to prepare insecticides. Late spring frosts however, in some situations often injure the young expanding shoots and recurrence of such disasters brings on a debility in the tree often ending in its death.

The walnut tree is met with in all Central Europe, Belgium, Spain, Holland, Italy, Great Britain, and as an ornamental tree as far North as the hinterland of the Moray Firth, but it does not thrive well too near the sea. It is widely distributed in France in the Charentes, the Dordogne, Isère, la Franche Comté, and Picardy. The tree yields a brown monospermatic nut which contains the almond or kernel, the raw material from which walnut oil is extracted. These kernels are not very rich in oil as they contain only 50 to 65 per cent. Ordinary walnut oil must not be confused with the oil of the American nut, which comes from carya nuts, a North American tree which is only used in Europe as an ornamental tree. The American oil is not much used except for lighting, is not an edible or an artists' oil. Experience has shown that fresh kernels when expressed yield a very turbid oil extremely difficult to clarify. It is only possible to extract the oil in a satisfactory manner after the nuts have been dried and stored for 3 or 4 months. By that time they will be ripe and the milky juice which they contain when fresh will gradually have disappeared. They must be preserved in a dry place, otherwise they will become rancid and mouldy. The kernels are crushed under a millstone. The oil is generally extracted in two stages. Pressing is begun in the cold so as to obtain virgin oil. The residue is moistened with lukewarm (tepid) water and again pressed, which enables 15 per cent. of a more ordinary oil to be extracted. Sometimes, however, the crushed almonds are hot pressed directly.

Composition of Walnut Oil.—Amongst the glycerides of walnut oil are those of lauric and myristic acids. Amongst the non-saturated acids are, according to Hazura, linoleic acid 80 per cent., linolenic and isolinolenic acid 13 per cent., and 7 per cent. of oleic acid.

The Constants of Walnut Oil Vary with its Age and its Degree of Rancidity.—Walnut oil is said to be difficult to preserve owing to its being prone to rancidity, but Halphen found no such tendency in Dauphine oils, which he had good reason to believe were pure from their origin and properties, which is necessarily of inferior quality to "virgin" oil.

Commercial Brands. 1. *First Pressed Oil.*—The oil from the first pressure is very pale or slightly greenish. It yellows as it ages. Its smell and taste are pleasant when fresh, and unpleasant after becoming rancid.

2. *Second Pressed Oil.*—This quality is of a more or less deep yellow, often brown, colour, and possesses an acrid odour and taste. Walnut oil is only slightly soluble in alcohol even boiling 1/60. On cooling it separates crystals which melt at 20° C. and solidify at 15° C.

Owing to its drying properties and its pale colour, walnut oil is used in the preparation of artists' paints and also for making certain inks used in wood-engraving. Large quantities are consumed in many countries as an edible oil. When rancid it is used in soap manufacture.

Analysis of Walnut Oil.—According to Halphen certain authorities are in error when they assert that walnut oil is not adulterated with linseed oil. Bellier has pointed out that poppy-seed oil was added thereto, and Halphen has frequently found walnut oil with cotton-seed, sesame-seed, and earth-nut oils. Crude in the beginning, these sophistications have gradually been improved, rendering the examination of this product tedious and delicate. The two sophistications most difficult to recognise consist in the addition of poppy-seed oil or linseed oil, which the colour reactions are powerless to detect, and which, on the other hand, approach so near to the chemical constants of walnut oil that it is difficult to prove their presence. It has already been pointed out that the formation of insoluble hexabromo-glycerides enables both drying oils and fish oils to be detected. Now the amount of insoluble bromine derivatives is very variable according to the nature of the drying oils, and in particular, the amount is far greater with linseed oil than with the others. On this is based a process of qualitative analysis by which it is possible to detect less than 5 per cent. of walnut oil in linseed oil.

The following table by Halphen shows the variations observed in walnut oil, after preservation for three years in cork-stoppered glass bottles only partially filled :—

TABLE SHOWING THE EFFECT OF STORING WALNUT OIL IN PARTIALLY FILLED CORK-STOPPERED BOTTLES FOR THREE YEARS.

Deviation by oleorefractometer . .	+ 33	+ 36	+ 34	+ 37
Iodine value	145·1	139·8	146·4	141
Acidity as acid oleic per cent. of oil .	—	1·27	—	1·05

Taking apparently sound walnuts which had been preserved for several years in the laboratory in a closed tinned iron vessel as the raw material from which to extract walnut oil, benzine only extracted very acid oils, the properties of which in no way corresponded with those of pure walnut oil as the following numbers showed. Sample I. was extracted from a first lot of nuts, using very little benzine. A persistent emulsion was formed, which only separated with difficulty. Sample II. was obtained by using more benzine, with the view of avoiding this emulsion :—

PHYSICO CHEMICAL CONSTANTS.	Sample I.	Sample II.
Deviation by the oleorefractometer . .	+ 28	+ 29·5
Iodine value	139·9	146·7
Acidity as acid oleic, per cent. . . .	32·99	13·63

In No. I. sample the alteration consists solely of hydrolysis with slight oxidation, which lowers the iodine value. In No. II. the hydrolysis is less pronounced, and the oxidation nil. These experiments show, therefore: 1. That oil prepared with fresh nuts undergo on storing no important alteration as regards refraction, iodine value, and acidity, and that a diminution in the iodine value corresponds to an increase of the refraction. 2. That oils prepared from old nuts are according to circumstances more or less acid, more or less oxidised, and that their constants are greatly altered by these modifications.

WALNUT OIL. FATTY ACIDS.

Observer.	Melting-point, ° C.	Solidification Point ° C.	Mean Molecular Weight.	Iodine Value.	Acetyl Value.
Benedikt and Ulzer .	—	—	273·5	—	7·6
De Negri and Fabris	16-18	—	—	150·05	—
Hübl. . . .	20	16	—	—	—
Kebler . . .	16-20	—	—	—	—

Hickory-nut oil resembles walnut oil very much, and is known as "American nut oil".

Wm. T. Brant says "oil of black walnuts is sometimes expressed, but is of little value". On examining the cold-pressed black walnut oil, the following physical and chemical constants were obtained. It is limpid, of a straw-yellow colour, possesses a pleasant, agreeable, walnut-like odour and taste, becomes turbid at 12° C., has a specific gravity of 0·9215 at 15° C., saponification number, 190·1 to 191·5; acid number, 8·6 to 9; ether number, 181·5 to 182·5; Hehner's number, 92·77; Reichert-Missel value, 0·00; iodine value, 141·4 to 142·7; melting-point of fatty acids, 20° C.

The drying qualities are excellent, equal, if not superior in this respect to linseed oil, leaving a tenaceous, flexible, transparent film. An artist, on using it, pronounced it a very satisfactory article for fine painting.

By a German process patented by Th. C. Graham, I. H. Kellog, and W. K. Kellog, D.R.P. 109,237, the oil is extracted from the nuts by roasting them between 150° and 180° C. (302° and 356° F.), the shelled kernel being made into a paste and mixed with water at 55° C. (32 litres of water to 100 kilogrammes of nuts when the oil floats to the surface).

Wood Oil. Standards for South China Wood and the Basis on which they were Elaborated.—Frank Brown, formerly Government analyst, Hong Kong, procured a quantity of genuine nuts from Wuchow, Kwangsi Province, and a certain quantity of oil was extracted by pressure only. Specimens of the nuts and of the

WALNUT OIL. TABLE OF CONSTANTS BY VARIOUS OBSERVERS.

Observer.	Density.		Solidification-point.	Saponification Value.	Iodine Value.	Maumené Test, ° C.	Refractive Index.
	° C.						
Allen	15	0·925-0·926	Thickens at − 15° C. Solidifies at − 27·5° C.	—	—	—	—
Crossley and Le Sueur	15·5	0·9259	—	192·5	143·1	101	64·8 in Zeiss's Inst.
De Negri and Fabris	15	0·9265	—	193·81-197·32	144·5-145·1	96	
Dieterich	—	—	—	188·7	147·9-151·7	—	—
Hazura	—	—	—	—	145·7	—	—
Hübl	—	—	—	—	143	—	—
Jean	—	—	—	—	—	—	+ 35 to + 36 Jean's Inst.
Kebler	15	0·925-0·9265	—	186-197	142-151·7	—	
Maben	—	—	—	194·4	—	—	
Maumené	—	—	—	—	—	101	—
Peters	—	—	—	—	143·3	—	—
Petkow	15	0·9255-0·9260	—	—	147·9-148·4	—	67-68 in Zeiss's Inst.
Saussure	12	0·928	—	—	—	—	
	25	0·919	—	—	—	—	
	94	0·871	—	—	—	—	—
Souchere	15	0·926	—	—	—	—	—
Valenta	—	—	—	196	—	—	—

extracted oil were sent to several authorities in various parts of the world. This pure oil had the following characters:—

Specific gravity, 15°/15°	0·9415
Iodine value	167
Saponification value	191
Heat test	12 minutes
Refractive index at 20° C.	1·5206
„ „ 15° C.	1·5226

At the time (1912) when the heat test was published there was no definite system of sampling the oil, and there were disputes, mostly with U.S.A. buyers, as to the quality of some of the consignments. These disturbances at last became so frequent as to seriously interfere with the export trade. The matter received the attention of the Association of Exporters and Dealers of Hong Kong, which, with the assistance of the local government, endeavoured to place the sale of this oil on a more satisfactory footing. From the characters of the pure oil extracted in the Government Laboratory and from the results of numerous examinations of oils, which had been accepted by buyers as genuine and thoroughly satisfactory, the following specification was drawn up for South China wood oil:—

"1. *Colour and Impurities.*—Chinese wood oil shall be pale in colour (according to season's production), merchantably free from foots, dirt, and moisture. The total impurities shall not exceed 1 per cent., but, unless otherwise provided for, impurities not plainly adulterations up to 5 per cent. shall not justify rejection, but allowance shall be made by sellers for such impurities in excess of 1 per cent.

"2. The refractive index of such oil shall not be less than 1·5204 at 15° C. Minus 0·0004 shall be considered the correction for each degree C. above 15 to 35° C., which should be applied to the refractive index when such is determined at temperatures between the points stated.

"3. The specific gravity at 15° C. shall not be less than 0·9400.

"4. *Heat Test.*—The oil shall satisfy the requirements of either Worstall's,[1] Bacon's,[1] Browne's ('Chemical News,' July 12, 1912—the period of setting in this heat test not to exceed 13 minutes), or Chapman's ('Analyst,' Dec. 1912) heat test.

"Any sample of South China wood oil that satisfies all the four tests above, namely, Nos. 1, 2, 3, and any one of the heat tests in No. 4, shall be considered to be good South China wood oil free from adulteration."

Particulars of this specification were sent by the Association to the responsible bodies in several countries, and at the same time opinions were asked as to any amendment desired. The replies received did not seem to indicate the necessity for any change in the specification as described above. The Hong Kong Government then undertook the sampling and examination of the oil. This consists in drawing about 1 oz. from each cask of oil offered for sale. The refractive index of each quantity is first determined, and any cask of oil with a refractive index under the specification figure is condemned for export purposes. The approved samples are then bulked and the gravity and heat test of the mixture determined. If the oil passes these tests the casks are sealed with lead seals, bearing a Government impression, and are then ready for shipment. The institution of this system of sampling has proved most satisfactory. It has restored the sale of the oil to its former dimensions, it has raised its quality, and has put an end to vexatious disputes and expensive arbitrations.

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[1] Described in the rules regulating business among members of the New York Produce Exchange in vegetable oils and fats not otherwise provided for as amended on September 5, 1912.

The following points may be useful to those examining this oil:—

When the gravity is determined at a temperature other than 15° C. it has been found that 0·00064 is the correction for 1° C. Thus a gravity of 0·9401 at 20°/15° C. is 0·9433 at 15°/15° C.

Proposed Standard Specification for Wood Oil and Linseed Oil.— Proposed standard specifications as follows were included in the report of the Committee on Protective Coatings, presented at the eighteenth annual meeting of the American Society for Testing Materials, held at Atlantic City on June 22 to 25, 1915:—

Raw Chinese wood oil shall conform to the following requirements:—

PHYSICO CHEMICAL CONSTANTS.	Maximum.	Minimum.
Specific gravity at $\frac{15\cdot5^\circ}{15\cdot5^\circ}$ C.	0·943	0·939
Acid number	6	—
Saponification number	195	190
Unsaponifiable matter, per cent.	0·75	—
Refractive index at 25° C.	1·520	1·515
Iodine number (Hübl, 18 hours)	—	165
Heating test (Browne's method), mins.	12	—
Iodine jelly test, mins.	4	—

CONSTANTS OF THREE SAMPLES OF JAPANESE OIL. (CHAPMAN.)

Locality.	Iodine Figure.	Density at 15·5° C.	Saponification Figure.	Refractive Index.	Time of Efflux in Seconds.
1. Wakasa	158·0	0·9377	195·2	1·5083	1·230
2. Idynmo	149·0	0·9400	193·4	1·5052	1·620
3. Locality unknown	151·8	0·9340	196·3	1·5034	—

Heat test, 2 hours at 250° C.—1, soft; 2, soft; 3, very soft.

Japanese wood oil has been said to be obtained from *Aleurites* *vernicia.*. But on the authority of Chapman it is quite distinct from the Chinese oil, being mostly obtained from *Paulownia Imperialis.* It is said to resemble the Chinese oil in composition and properties but it does not solidify on heating to a high temperature.

The American Consul in Japan in his report (105, 1917) states that "An oil used in Japan in the manufacture of oil, paper, and paints and for illuminating purposes, is obtained from the fruit of a tree *Aleurites Cordata* ('Oil Paulonia'). This tree had been growing wild in Japan until four years ago, when it was for the first time on a very small scale cultivated for commercial purposes. The use of the oil paulonia product has been known in Japan for a long time but has not yet acquired any commercial importance. The oil is extracted by the most primitive methods, drying, pounding, steaming, and crushing by producers on their farm. Japan's output is about 1,500,000 bushels of nuts annually, from which 238,300 gallons of oil worth $110,000 is obtained. None of this oil is exported. Shells and kernels crushed together give 36·1 per cent. of oil, while 48·85 of oil is obtained from the kernel" (U.S.A. *Consular Report*).

The Chemical Composition of Wood Oil Fatty Acids.—Wood oil contains from 10·4 to 10·6 per cent. of glycerol, 96 per cent. of insoluble fatty acids, and about 0·5 per cent. of insoluble matter (Jenkins). Cloez was the first chemist to examine wood oil. He found the fatty acids to contain a liquid and a solid portion. The first consists of normal oleic acid. The solid fatty acid, pressed through filter paper free from the entrained oleic acid and then crystallised from alcohol, melts at 48°. Its combustion results and the analyses of its salts pointed to the formula $C_{17}H_{30}O_2$. Cloez named this acid elaeomargaric acid and found 72 per cent. of it in wood oil. He found that it was very unstable, and that in the air it rapidly absorbs oxygen. Long after the date of Cloez' researches, L. Maquenne examined solid wood oil fatty acid *de novo.* He termed it elaeostearic acid. On oxidation by $KMnO_4$ (not in alkaline solution) he obtained from it azelaic acid and *n* valerianic acid; instead of $C_{17}H_{30}O_2$ he found the formula $C_{18}H_{30}O_2$. The iodine figure of wood oil indicates that the greater proportion consists of an isomer of linoleic acid; but Walker and Warburton, in brominating wood oil, in one sample found no hexabromide insoluble in ether, in a second sample only 0·38 per cent. T. Kametka found that elaeostearic acid is not an isomer of linolenic acid but of linolic acid, $C_{18}H_{32}O_2$. For the acid crystallised from alcohol he only found the melting-point of 43° to 44° C. By brominating it in acetic acid solution he obtained a tetrabromlinolic acid, melting-point 114° C., and with the Hazura oxidation process, sativic acid, tetraoxystearic acid and dioxystearic. Finally he states that the acid still contained oleic acid, hence its low melting-point. Kitt found a higher melting-point, 48° C., and that stearoleic acid with three linked bonds has this melting-point. On oxidation by nitric acid he only obtained azelaic acid, with the Hazura oxidation process a very small quantity of dioxystearic acid, also a water soluble acid melting in the crude condition at 97° to 102° C. S. Fokin, by electrolytic reduction, obtained stearic acid with the nucleus C_{18}. A. Rathje extracted from wood oil both fatty acids, according to Warrentrap. The lead salt of elaeomargaric acid is insoluble in ether, the extraction is not at all sharp or well defined, as it is shown that Rathje found for the oleic acid instead of an iodine value of 90, one of 93 and the low melting-point of 43° to 44° C. Finally he found that wood oil fatty acids contains 75 per cent. of elaeostearic acid and 25 per cent. of oleic acid, whilst Cloez data gives 72 per cent. of solid fatty acids therein.

R. Majima throws some light on the constitution of elaeostearic acid, the melting-point of which he gives as 48° to 49° C. (118·4° F.). In an atmosphere of carbonic acid under a pressure of 12 mm. the elaeostearic acid boils leaving, about 235° C. (455° F.), 11 to 14 per cent. of a brown amorphous mass. The purified acid was dissolved in chloroform and ozonised in a freezing mixture. The result was a yellowish semi-solid, which on combustion gave an ozonide of the formula $C_{18}H_{32}O_8$. On boiling with water it solidified. The water showed the H_2O_2 reaction, and there was isolated therefrom valeric aldehyde and the semi-aldehyde of azelaic acid, *n* valerianic acid, azelaic acid. The formula of elaeostearic acid is therefore

$$CH_3(CH_2)_3CH(CH_2)_2CH \,.\, CH(CH_2)_7COOH.$$

It has, therefore, like linoleic acid, the central double bond, not between the 6 and 7, but between the 5 and 6 group.

TABLE SHOWING THE CHEMICAL AND PHYSICAL CONSTANTS OF TWO SAMPLES OF CHINESE WOOD OIL AND THEIR FATTY ACIDS. SAMPLE I. DIRECT FROM CHINA; II. FROM FIRM OF CARLOWITZ IN HAMBURG. (KITT.)

Oils :—	I.	II.	III.	
Specific gravity at 15° C.	0·9413	0·9439	II. solidified by light	
Saponification value .	190·7-191·0	190·9-191·4	191·0-191·8	
Iodine value . . .	157·5-158·4	154·6	155·2-161	
Acid " . . .	3·9	6·95	—	
Fatty Acids :—	**I.**	**II.**	**III.**	**IV.**
Melting-point . .	35-39·5° C.	35·5-40	41-46	Blown at 150-180° C., 2 hours
Neutralisation value .	197·3-197·8	196·4	198·8	199·5
Yield of insoluble . .	82	85	—	—
Iodine value . . .	—	169·5	107·6-108·4	—

The chemical and physical constants of the above two oils are given under oils I. and II. That given under oil III. is oil II. solidified by exposure to light. The data given under fatty acids I. and II. refer to the original untreated oil. The figures under fatty acids III. refer to fatty acids from oil II. after the oil had been heated in a porcelain basin, and stirred by a thermometer until at 282° C. it solidified. The gelatinised mass only dissolved partially in benzene, but alcoholic potash completely saponified it. The separated fatty acids were dark brownish-yellow, with green fluorescence. After some days they solidified to a crystalline mass.

W. G. Scott states that: "Assuming the viscosity of raw linseed oil as 4·000 compared with that of water as 1·00, wood oil will have a viscosity of about 20, and the oil is really about five times as thick".

Wood Oil Solidifying-point.—The fresh oil solidifies at + 2° to + 3° C., but does so only after the oil has been exposed to the freezing mixture for 4 hours at least. Oil kept for six months by De Negris and Sburlati by cold expression began to solidify at − 18° C. Again Cloez cooled wood oil to − 18° C. without it becoming turbid, and Jenkins confirmed Cloez' results with his two samples.

Index of Refraction.—The refractive index of wood oil was found by Jenkins to be 1·503 at 19° C. with sodium light.

Optical Deviation.—Nil.

Viscosity.—The two samples of oil analysed by Jenkins took respectively (1) 858 and (2) 1453 seconds to flow from Redwood's viscometer at 60° F. An equal volume of water required 28 seconds, whilst pure rape oil took 470 seconds. There is an unaccountable difference between Jenkins' results, which Jenkins explained might be due to partial polymerisation of one of the samples.

The Physical Properties of Wood Oil. Specific Gravity.—Wood oil has the highest specific gravity, viz. about 0·940, of any vegetable oil, except castor oil or croton oil. This high gravity is about 0·008 higher than ordinary raw linseed oil, and even approaches that of fire-boiled oil, or to be more exact, it would be better to say that the specific gravity of fire-boiled oil approaches that of wood oil. The specific gravity of all Chapman's samples are more or less above 0·940, and not one of them under it. But De Negris and Sburlati both report samples much under 0·940 (0·936). De Negris and Fabris 0·9343 to 0·9385. The wide differences in the recorded gravities are perhaps due, on the one hand, to the oils not being derived from the same species of *Aleurites*. Oxidation also increases the gravity.

The odour of the Chinese wood oil is a very peculiar one and adheres to the dry coating made with it; it adheres so strongly that it is plainly noticeable even after oilcloth-like goods dried in hot air for months, the same as oilcloth will always, even after years, smell of linseed oil. Naturally, this peculiar lard-like odour also shows itself with the varnishes produced from the oil, and it therefore becomes necessary to remove it by some process.

In the manufacture of leather, waxcloth, and linoleum, an odourless and cheap varnish, which will dry very quickly, is a prime desideratum. Until lately dry linseed oil was the favourite substance used. Of late, however, wood oil has been tried, and gave highly satisfactory results in respect of drying qualities, but had the great drawback of possessing a very disagreeable smell, due to its auto-oxidation products which are more and more intensive in the air. The following four methods were tried by Ulzer with a view of removing this only obstacle to its replacement of drying oil which is considerably dear: 1. Extraction of the odorous bodies by solvents. 2. Extraction of the odorous bodies (which are possibly aldehydes and ketones) by sodium bisulphite. 3. Treatment with substances at the same time bleaching and deodorising. 4. Treatment with superheated steam.

1. The solvent principally tried was alcohol, in strengths of 20 and 40 per cent. When the oil had separated out after having been shaken up with the spirit, it was dried in a stream of warm carbonic acid. It is true that the disagreeable smell was diminished, but the results were unsatisfactory, even without regard to the cost of the method. 2. *Deodorising by Reducing Agents.*—This method was tried by boiling the oil for 6 hours with twice its volume of a 10° B. solution of sodium bisulphite with a reflux condenser. The oil was then washed with water from the excess of bisulphite. Its evil odour was not then appreciably less. This shows clearly that the malodorous substances present are neither ketones nor aldehydes. 3. *Deodorising by Animal Charcoal.*—Animal charcoal, silicate of magnesium, and the residues of the manufacture of potassium ferrocyanide were tried, without success. 4. *Deodorising by Blowing with Superheated Steam.*—By this method very interesting results were got. The first trial consisted in blowing superheated steam at 130° C. through the wood oil for 8 hours. The nasty smell was perceptibly lessened, but the oil partly solidified on cooling. When the steam was used at 165° C. a marked

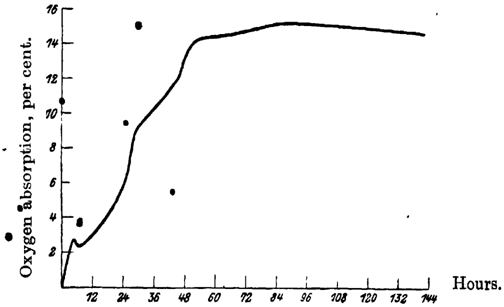

FIG. 114.—Oxygen absorption, per cent. by weight of wood oil.

diminution of the bad odour took place, even in 2 hours, and in 5 there was very little smell of any kind, what there was being much like that of linseed oil. In 12 hours the oil had begun to deposit and had regained some of the disagreeable odour. This recrudescence of the smell was, however, only slight when the oil was cooled without contact with air, showing that the action of atmospheric oxygen has probably something to do with the formation of the evil-smelling substances. 5. *Deodorising by Air Blowing.*—Attempts to conceal the bad odour were made, especially with birch-tar oil, but were quite unsuccessful.

Bang and Ruffin claim to completely deodorise the oil by blowing for 6 to 8 hours at 50° C.

CHEMICAL AND PHYSICAL CONSTANTS OF WOOD OIL.

(*Refractive Index*, 1·503.)

Observer.	Density at 15° C.	Solidification-point.	Helmer's Value.	Saponification Value.	Iodine Value.
Davies and Holmes .	0·940	—	—	211	—
De Negri and Sburlati	0·936	—	—	156-172	159-161
Jenkins . .	0·9343- 0·9385	below - 17°C.	96-96·4	194	149·7- 165·7
Ulzer	—	—	—	194	162
Williams . .	0·9415- 0·9432	—	96·3-96·6	190·7 196·1	155·4 165·6

FATTY ACIDS.

Observer.	Melting-point, ° C.	Solidification-point, ° C.	Iodine Value.	Heat of Bromination.
De Negri and Sburlati .	43·8	31·9	159·4	—
Jenkins	30-37	34·0	—	21-22·1
Williams	40-49·4	37·1	144·1-150·1	—

Until lately the only literature on wood oil consisted of short papers by Davies and Cloez, but a large number of workers have recently busied themselves with this product, such as Holmes De Negri and Sburlati, Jenkins, Williams, Fraps, Jean, Kitt, Milliau, Chapman and others.

Their results are so far given in the table.

A. C. Chapman has recently given the analysis of seventeen samples of Hankow wood oil, which are reproduced in the following table:—

CONSTANTS OF WOOD OIL (CHAPMAN).

Sample No.	Iodine Value.	Specific Gravity at 15·5° C.	Saponification Value.	Refractive Index at 20° C.	Time of Efflux, Seconds.	Heat Polymerisation Test, 1 Hour at 280° C.
1	169·9	0·9419	190·6	1·5207	2178	Very hard.
2	168·4	0·9406	193·8	1·5181	1636	Hard.
3	166·5	0·9425	194·3	1·5190	1946	Fairly hard.
4	166·4	0·9417	193·0	1·5170	1880	,,
5	168·8	0·9430	195·6	1·5195	2017	Very hard.
6	170·0	0·9440	194·5	1·5180	1849	Hard.
7	168·6	0·9416	193·0	1·5150	—	Fairly hard.
8	171·0	0·9414	192·0	1·5176	—	Hard.
9	109·7	0·9437	194·1	1·5170	1997	,,
10	173·0	0·9420	192·5	1·5165	1722	,,
11	176·2	0·9417	192·0	1·5168	1605	,,
12	172·6	0·9420	196·0	1·5180	1740	,,
13	174·2	0·9427	194·0	1·5182	1690	,,
14	173·7	0·9420	195·0	1·5194	1820	,,
15	172·8	0·9440	194·0	1·5193	2047	,,
16	169·5	0·9420	195·2	1·5160	1804	,,
17	169·0	0·9433	195·2	1·5187	1820	Very hard.

There appeared recently a paper by Dr. C. D. Holley and J. P. Richards upon Chinese wood oil, in which they state that examination of a large number of samples of this oil during 1916 has proved that a high proportion were adulterated, but those which were passed proved to be very uniform in quality, the "turning-point" (i.e. abnormal dispersion) being 20 to 21, which is considerably higher than those shown during the three preceding years. The authors state that if the "turning-point" and the acid value of an oil be known it is comparatively easy to predict its behaviour in the varnish kettle, the high "turning-point" oils being by far the best for this treatment. The "turning-point" test, as worked out by the authors, is regarded by them as far superior to any form of heat test or other method of testing quality. The improvement of testing, especially the fact that the purity of an oil can be put on a numerical basis, led the authors to the conclusion that probably still purer oils having higher "turning-points" might be obtainable, perhaps approximating to the pure oleomargaric acid glyceride, which, according to their investigations, has a turning-point of 25 to 25·5 at 25° C. With this idea in view, several samples of the purest wood oil obtainable were got direct from China, and on examination the authors' view proved to be entirely correct, as shown by the following table:—

	Acid Value.	Turning-point at 25° C.
1	7·3	23·6
2	2·5	20·5
3	3·7	23·9
4	7·6	22·3
5	1·4	24·9
6	6·6	22·5
Average . . .	—	23·0

A comparison is also made of three of these oils with an average 1913-15 oil by a slightly modified Browne heat test, the temperature of heating being 282° C.:—

	Oil	Turning-point	Acid Value.	Heat Test, Time of Solidification.
1	1913-15	15·6	2·0	10 min. 55 sec.
2	1916	20·5	2·5	10 min.
3	Special	23·6	7·3	10 min. 15 sec.
4	,,	23·9	3·7	8 min. 55 sec.
5	,,	20·5	2·5	10 min.

It is clear from these tests that the time required for gelatinisation varies inversely as the turning-point, and, with the turning-point remaining constant, the time varies directly as the acid value. The behaviour of the oil in the kettle thus depends mostly upon the turning-point and to a lesser extent on the acid value. Now that adequate methods of examining Chinese wood oil have been devised, there is every reason to believe that better qualities of this oil will be supplied than was formerly the case, but the writers are of opinion that the methods laid down by the American Society for Testing Materials are inadequate, seeing that they allow oils adulterated to as much as 15 per cent. to be classified as pure oils.

A quarter of a century ago Chinese wood oil or tung oil from *Aleurites Fordii* was almost unknown to European or American varnish-makers and oil-boilers. Two decades ago it came more often than prior thereto on the European markets, and eventually it reached America, where it was adopted forthwith, and so far made its way that much of the special technical literature of the subject, if not the whole, is of American origin. Both in America and Great Britain importers have vied with one another in striving to find new markets for the oil, yet there are many interested persons who even now have no adequate conception of the peculiarities and all-round usefulness and possibilities of this oil. For three decades its peculiarities have been investigated by many chemists, and so successful have these investigations been that at the present day it may well be said that these peculiarities have all been brought under control. The unruly oil has been tamed. Abortive attempts have been made to acclimatise the tree from which the nuts that yield the oil are obtained. The experiments somehow did not succeed. In China it is used as an illuminant and for fuel, but its consumption is chiefly as a varnish for boats (junks), houses, and furniture. It is also largely used in the varnishing of the native umbrella, and in the manufacture of waterproof cloth, whilst it is practically a necessity in the manufacture of the finest silks. Of late years it has even been used in the building of forts, forming with lime, sand, and clay a material almost as tough as granite. In the western provinces the oil is adulterated to lessen its cost and to bring it into consumption for "coarser" purposes. Owing to the distance which the product has to be brought to export ship, the great cost of repacking (an absolute necessity) and freight, its lay down price is heavy.

The oil, particularly when freshly pressed, is somewhat poisonous, so also are the nuts and kernels. This is well known to the Chinese. The cake is therefore calcined to lamp-black. It cannot very well be burnt to ash, but what is done with the charred residue is not known; possibly it too is used in making India ink. At any rate, the cake cannot be used as a feeding-stuff, although it might possibly be used as a manure.

According to a United States consular report, the Chinese oil tree, to which the writer of that report erroneously gives the botanical name of *Aleurites Cordata*, belongs to a family very common in China, to which the name of tung is given. The oil tree itself is called *Ying-tzu-tung*, so called after the shape of its fruit, ying, meaning bottle. It is a small tree, growing to a height of 10 to 15 feet in stony ground and chiefly in Hunan, Hufeh, and Szechuen. The tree has been successfully acclimatised in the Southern Shan States, between 1500 and 3000 feet in altitude, and to some extent also in Burmah, Assam, Sikkim, and Nepal. It is frequently met with near Buddhist monasteries, though in some localities it appears to have escaped into the neighbouring jungles. It is said that in the Southern Shan States the tree grows quickly and is easily propagated from seed. A tree 5 years old attains a height of about 16 feet, and when 8 to 10 years old comes into full bearing. The fruit ripens in the Shan States about October or about 3 months later than the fruit of the candle-nut tree *Aleurites triloba*. It is believed that, were a remunerative demand to arise, in a very few years the supply of wood oil from the Shan States would be limitless. In China the fruits, which are gathered in August and September, contain five to seven large poisonous seeds. Of the Japanese wood-oil tree it is said that the tree flowers at the end of May or beginning of June. The fruit ripens in autumn. Three to five seeds are contained in each fruit, which is something like our walnut. They afford an oil to the extent of 37½ per cent., which is cold-pressed in ordinary practice to the extent of two-thirds of the possible yield. This oil is known in Japan by the name of *Dokuyenoabura*, and serves for filling the pores of wood before it is coated with lac, or it is used when desired to protect wood against moisture.

From information procured from the Southern Shan States it appears that the tree is fairly plentiful and the oil regularly prepared although the demand is but limited. It has been estimated that the nuts of each tree might yield 50 ounces of oil. The kernels are first pounded, then steamed in a basket placed over the mouth of a pot in which water is boiled. The basket is next placed within a piece of bullock's skin, and the whole deposited in the oil-press and compressed. The oil escapes into a vessel placed below for its reception. It is much more highly appreciated than candle-nut oil from *Aleurites triloba*. It is known in Kengtung as Makyauhkai and near Fort Steedman as Kangyin. In China the oil is said to be obtained in a similar manner to earth-nut oil. The nuts are collected, dried, and placed in an ordinary Chinese reiskwo (a shallow iron vessel 2 feet in diameter) which is put over an open fire. They are then ground to powder by stones and pressed in wooden presses. The substance that is left in the press is afterwards carefully calcined, and the soot so obtained is used in the manufacture of the so-called India ink or Chinese ink.

ANALYSIS OF WOOD OIL NUTS.

	Kernels.		Shells.
Water	3·98	6·24	14·40
Crude protein	19·62	21·57	2·50
„ oil	57·42	47·80	0·04
Nitrogen extract	12·68	17·27	27·62
Crude fibre	2·68	3·02	50·64
Ash	3·62	4·10	4·80

The nuts when cold-expressed yield about 35 per cent. of a clear colourless oil and about 44 per cent., on extraction with a solvent, carbon disulphide. De Negri and Sburlati give 53·25 as the yield by extraction by solvents and 42 per cent. by cold expression. Hot expression gives a better yield at the expense of the quality of the oil, which is brown with a piercing unpleasant smell, and is not so much appreciated on the market.

Cloez states that the oil extracted by him was odourless, but the oil obtained by De Negri and Sburlati by cold expression had a peculiar smell, like that from second-pressed castor seed.

The crushing of wood-oil nuts has unfortunately not yet been done on a manufacturing scale in Europe, as there seems to be some doubt both of regularity of supply and value of press-cake.

There are no reliable statistics of the Chinese wood-oil nut harvest.

In 1899 Hankow and other Chinese ports exported about 30,000 tons of wood oil, and it is considered that China herself uses double that quantity. This would make the total output of oil about 90,000 tons, and of nuts about 160,000 tons. The nuts themselves are not exported. It seems fairly certain, however, that a real demand would soon be followed by an increase in the cultivation of the nut. The well-known variability in the quality of wood oil is due on the one hand to its coming from different species of *Aleurites*, which are as yet imperfectly known, but many of which are confused with *Aleurites Fordii*, the true source of Chinese wood oil, and on the other hand to the very primitive manner in which the Chinese extract the oil. The exporters at Hankow recognise three sorts: pai-yu, hsin-yu, and hung-yu, but do not themselves know whether the differences are due to different sources of origin or to one being a first, another a second pressing, or one being hot pressed and another cold pressed, or other differences having existed in their treatment. The investigations, the results of which are given below, were carried out with a small quantity of nuts, of which the exact locality of origin is unknown, except that it is Chinese. A slightly modified form of arachis-sheller was found to extract the kernel perfectly, and the kernels were 52 per cent. of the weight of the whole nut. The shells are of no value, and this is a matter of great importance, for it is evident that freight would be saved if the nuts were shelled in China. It is true that the kernels are very prone to become rancid when deprived of the protection of their shell, but they would not suffer during the voyage if packed air tight. The kernels gave 58·7 per cent. of oil by extraction with ether. A pressure of 350 atmospheres on the other hand, at 28° C., only gave 43·0 per cent. The residue from this pressing, when broken off and again subjected (between rollers) to a pressure of 350 atmospheres at 65° C., gave 10·7 per cent. of the 15·7 per cent. still remaining. Thus the total yield was 53·7 out of a possible 58·7 per cent. Hence the yield reckoned on the whole nut is 22·36 per cent. on the first pressing, and 5·56 per cent. on the second, with 24·08 per cent. of oil cake. The oil from the first pressing was a pale yellow, and that of the second a pale orange, and more viscid than the first. The constants of both oils agreed substantially with those already obtained by other investigators. It was found, however, that by picking the nuts before pressing and rejecting any that showed any sign of rottenness, the acid number of the oil of the first pressing could be brought down to 0·9. The oil has also no longer the disagreeable characteristic wood-oil odour, and can be kept for weeks in a well-stoppered bottle without developing it. If exposed to the air, however, it quickly acquires it. This seems to confirm Ulzer's opinion that the development of the smell is a result of oxidation. But possibly the oil could easily pass through a sea voyage, in well-filled and closely stoppered vessels, without acquiring any of the disagreeable odour. The press-cakes are very poisonous, and contain 53 per cent.

of protein and 12·1 per cent. of fat. The Chinese use them for manure, and also burn them for the manufacture of lamp-black. If some means could be discovered of extracting their poisonous ingredients the high percentage of protein which they contain would make them an excellent fodder.

To the importers the package question has been a serious one, as much loss resulted in transportation, the loss by leakage amounting to as much as one-third. In order to overcome this, one firm of New York importers sent staves, heads, and hoops for 6000 barrels to Hankow to be put together, and filled with the oil there. With American firms entering into competition in its importation, improvements in service and more regularity, in the way of supplies, may be looked for, the shipping and importing having heretofore been in German and English hands exclusively. The quality of the oil is defined by the term Hankow and Canton China wood oil, the latter commanding higher prices by 10 per cent.

Light alone, without air, is said to cause wood oil to dry. Exposed to light for some time, the length of which depends upon the time of the year, wood oil slowly becomes solid. At first there is a deposition of solid stearine-like particles, but in time the whole mass solidifies; at the same time the oil loses its yellow colour and turns white. On heating, the solid melts, but reforms on cooling. In thus solidifying on exposure to light, tung oil differs from other oils. Poured in a thin film over a glass plate, wood oil takes about 2 days to dry, being, therefore, quicker in its drying capacity than raw linseed oil, which takes about 3 days to dry. Unlike other drying oils, wood oil does not dry from without inwards, but the process goes on simultaneously through the thickness of the coat of oil. The dry film left by Chinese wood oil has a different appearance to that left by linseed oil; it is duller and more opaque, which is rather against its use in painting, and, besides, the coat or film is crinkled and rough. Linseed oil leaves a smooth and bright film. This opacity appears to be due to the presence of large percentages of mucilaginous and albuminous matter, and at low temperatures the oil becomes waxy, settling out organic salts similar to the stearates. On account of this peculiarity it cannot, like linseed oil, be used in the raw or crude state and requires special treatment, but, even then, it must not be considered as a substitute for linseed oil for use in paint, and in the manufacture of varnish, but rather as a valuable adjunct to prompt thickening and other important drying properties.

Wood oil is well adapted when properly handled for mixing with linseed oil, the latter component giving elasticity and the former hardness and resistance, as well as an increase in drying properties. When heated to 200° it thickens; at 260° to 280° C. the oil gelatinises, but the jelly does not stick to the fingers. It should therefore not be heated above 180° C.

Heating Chinese wood oil appears to have no material influence in accelerating its drying power.

The behaviour of Chinese wood oil under heat is peculiar, and sharply differentiates it from other oils. Maintained at a temperature of 212° F. for some days, it slowly gelatinises, the jelly, which is formed, not being liquefied by heating. Heated up, it, like all other oils, becomes thinner and more limpid; it does not darken so much in colour as linseed oil; heated to about 550° to 560° F., it sets almost immediately into a transparent jelly, which is permanent on exposure to the air, and has an appearance and consistency recalling that of india-rubber. This jelly is not melted by subsequent heating, and it is quite insoluble in hot oil, benzol, turpentine, petroleum spirit, alcohol, and similar solvents.

Boiled wood oil, if prepared at a low temperature and without the addition of driers, is always more viscous than linseed oil. In laying it on a surface, therefore, it is more difficult to get a thin layer. A surface varnished with wood oil which is too thick, has more of the varnish on it than is necessary. The surface of this layer dries quickly, and having behind it the still liquid portion, is enabled to draw together and wrinkle. This does not happen when the layer is thin enough to dry through. For this reason, in using wood oil varnish, it is essential to note its thickness, and if necessary thin it down with turps. The same thing may be noticed with linseed oil varnishes, if not properly thinned, or too thickly laid on. Too large a proportion of driers also causes wrinkling for the same reason as the excess of driers thickens the oil.

TABLE SHOWING THE ACTION OF HEAT AT DIFFERENT TEMPERATURES AND FOR DIFFERENT PERIODS OF TIME ON THE CHEMICAL CONSTANTS OF WOOD OIL, AND OF WOOD OIL MIXED WITH A CERTAIN PROPORTION OF LINSEED OIL.

	Heated, Hours.	° C.	Free Acid, per Cent.	KHO per 1000 Grammes.	Iodine Absorption, per Cent.
Wood Oil, I.	—	—	7·1	175·9	161·9
"	2	150	3·9	185·8	162·2
"	5	150	1·1	185·3	154·5
"	9	150	0·6	180·1	142·2
"	9¾	Solid	—	195·4	—
Wood Oil, II.	—	—	5·6	193·9	160·7
"	2	150	5·1	193·4	157·8
"	5	150	2·6	190·4	143·5
"	6	Solid	—	187·2	—
Wood Oil, I. + 25 per cent. linseed oil	—	—	6·0	177·9	172·6
" " "	2	180	3·1	188·1	151·7
" " "	5	180	1·1	187·3	136·1
" " "	5½	Solid	—	191·6	—
Wood Oil, II. + 25 per cent. linseed oil	—	—	4·8	192·3	165·2
" " "	2	180	2·1	192·7	147·3
" " "	4	Solid	—	—	—

The oil does not appear to possess much solvent properties for driers, especially for the linoleates and rosinates of lead and manganese. Driers may be prepared from the oil preparations of lead and manganese, similar to linoleates, which act more efficiently with linseed oil than any other preparations. The use of these preparations has been described in an English patent, where they are called "tungates".

On heating wood oil with rosin only, the acidity of the latter is affected, but that is greatly decreased, whereas, the acidity of a mixture of linseed oil and rosin is increased.

TABLE SHOWING DECREASE OF FREE ACID PER CENT. IN HEATING A MIXTURE OF ROSIN AND WOOD OIL.

	Free Acid, per Cent
Wood oil	11·0
,, heated to 200° C.	10·7
,, ,, to 245° C.	7·5
Rosin heated to 300° C.	298·2
,, and wood oil heated to 300° C.	65·4

In heating wood oil for the purpose of making varnish, it must always be borne in mind that the temperature must never exceed 180° C., as the oil then gelatinises and will not mix with the other ingredients of the varnish. But with care, the result is invariably extremely good. If the oil be heated with a drier and then thinned with French oil of turpentine, the result is always good, although prolonged stirring is necessary. Experiments have shown that borate of manganese is not a suitable drier for wood oil, but borax answered extremely well. Mixtures of wood oil and linseed oil were also tried; the varnish dried in 24 hours on glass, and after a little became perfectly hard and transparent. But when the dried varnish was exposed to the weather, damp, dew, and rain, loosened its adhesion—which was, however, fully restored by exposure to dry air or sunlight. On wood, the varnish resisted very much better, especially when mixed with zinc white. The following are typical experiments made on wood oil: (*a*) Fifteen pounds of wood oil having been warmed up, 5 lb. of lead acetate were added to it, a little at a time, the heat being kept up until solution was complete. Ten pounds of gum resin were then added, and when this was melted the varnish was thinned with 10 lb. of French turpentine oil. The varnish so prepared dries in 10 hours. A coating of it on tinplate, which was then steeped in a solution of sodium carbonate for 24 hours, was not affected, except as regards its colour. The latter was made somewhat paler, but the adhesiveness of the varnish was not diminished. Varnishes made with linseed oil and subjected to the same treatment were practically destroyed by the alkaline solution, and could be afterwards removed without difficulty. (*b*) Ten pounds of rosin were melted up with 5 lb. of borax. On to this mixture 15 lb. of wood oil were poured. The whole was then heated up and mixed with 20 lb. of French turpentine oil. The varnish thus obtained dried rapidly for the first hour, but as soon as the turpentine had all disappeared the rate of drying became very much slower, and after 15 hours the varnish was still sticky. This seems to indicate a good varnish for gilding. The varnish was completely dry in 48 hours. (*c*) This experiment resulted in a very good varnish, which, however, requires very great care in its preparation. Fifteen pounds of wood oil were mixed with 2 lb. of "gum" resin and driers, and the mixture was heated to frothing. Then 10 lb. of rosin were added, and when the latter was melted the heating was continued to as high a temperature as possible without gelatinising the wood oil, careful stirring being kept up until the liquid began to stiffen. The vessel was then removed from the fire, and 40 lb. of French turpentine oil were carefully and thoroughly stirred into its contents. The varnish so prepared looks a bit turbid at first, but becomes quite clear within 14 days. Spread on glass, it dries to a hard and elastic coat in 8 hours or 10 at the most, and on wood it dried in 5 hours. When applied to glass it had a fine lustre, and was entirely transparent. Any resin can be used for this varnish provided its melting-point is below 180°, as is, for example, the case with soft manilla copal. (*d*) The varnish made by this process would suit admirably as a thinning medium for stiff paint. The ingredients were 15 lb. of wood oil, 15 lb. of linseed oil, and 4 lb. of rosin. After the usual heating, the varnish is thinned with 20 lb. of French turpentine oil. The varnish so prepared dries within 24 hours. As above mentioned, its adhesion is destroyed by damp. In spite of containing linseed oil it always retains a whitish tinge.

The peculiar property of wood oil for thickening to a jelly-like substance when heated to about 300° C., and its tendency to dry with a flat, "crawly" surface are well known, likewise the removal of this objectionable property by the use of rosin or linseed oil. It may be used alone if very carefully treated, but must be handled with great caution, or mishaps will occur. Its present crude method of extraction seems to give a rather variable product, and it cannot be always depended upon to behave at all times in exactly the same way.

Manganese rosinate when boiled with wood oil in generous proportion gives very satisfactory results in preventing flatting and crawling. The following formula is recommended as giving a cheap but very fine wearing varnish of good colour:—

250 lb. China wood oil, heat to 200° C., allowing no increase above this temperature. Add 8 lb. manganese rosinate fused and boil to desired consistency at 200° C. Add 80 lb. hardened rosin fused. When cooled to 125° C. (257° F.) add 250 lb. benzine.

If water-white rosin is used it will give a still paler varnish. If properly made this varnish will dry quickly and hard, and stands outside exposure in a remarkable manner, though the percentage of rosin is small. Hard zinc rosinate may be used instead of hardened rosin to produce a quicker, harder drying varnish, and is said to give splendid results. A much cheaper varnish is produced by the following formula:—

250 lb. China wood oil.
8 lb. manganese rosinate.
400 lb. hardened rosin.
450 lb. benzine.

Treat as before.

This cheap grade varnish, it is claimed, will stand outside exposure for two or three months before showing any signs of deterioration. It has a splendid gloss, and on the whole is very satisfactory looking at the low cost.

An excellent grinding japan may be made as follows:—

250 lb. China wood oil heated to 200° C.

Add 20 lb. manganese rosinate, and heat at 200° C. to the desired consistency.

Add 100 lb. zinc rosinate, heat until thoroughly incorporated, withdraw from fire and allow to cool.

Add 400 lb. of turps.

A good cheap furniture and rubbing varnish can be made by mixing 2 lb. of the above with 1 lb. medium heavy gloss oil, and a satisfactory floor varnish by mixing 4 lb. of the above with 1 lb. of gloss oil.

The relative proportions of turpentine or benzine as thinners in the above varnishes can be varied at will, but on the whole, they contain so great a percentage of oil, that a large proportion of thinners is not necessary to make them brush nicely and flow smoothly.

The peculiar flatting property of wood oil has been utilised to make flatting varnish without the use of wax. A very prominent American brand is produced by the following formula: Emulsify 10 gallons China wood oil by boiling in an ordinary varnish pot with 11 gallons water, in which is dissolved 8 lb. soda ash and 1 lb. granular caustic soda. Dissolve in a separate vessel 20 lb. alum in 20 gallons water. When the oily mass drops heavily from the stirrer, add 22 lb. rosin, powdered so as to melt quickly. After thorough incorporation, add the alum solution, which will cause the whole mass to separate on stirring. Allow to stand overnight, run off all the water possible, heat until the remainder is driven off, and dissolve residue in 70 gallons turps. To produce the flatting varnish, mix this with equal parts of manila or kauri varnish. Many technical writers agree that this oil will become of greater importance in the near future; too much stress cannot be laid upon working it carefully and with intelligence; the peculiar properties make its use a constant menace otherwise. Despite the objectionable features of this oil, it has been used with great success by some, and those varnish makers, who have not taken it up, or have been unable to manipulate it satisfactorily, are gradually finding themselves outdistanced by their more successful rivals in the manufacture of such varnishes.

After much money and time has been expended in researches and experiments, and millions of pounds of the oil wasted, the general conclusions arrived at is, that this oil requires boiling with lead or manganese compounds, but in a different way from that of boiling linseed oils, which can be raised to a temperature of 320° C. (588° F.), while China wood oil must under no consideration be heated by itself alone to over 180° C. (356° F.). While some of the oil, off and on, may stand a temperature of 200° C. (392° F.), it is liable to go with great rapidity into a jelly, that is of no use whatever, even at a much lower point. The safest way to treat the oil and make it lose its opacity on drying is to heat it in a portable pot over a moderate fire, to 160° C. (320° F.), and as soon as the temperature reaches 180° C. (356° F.) remove the pot from the fire and stir into the still simmering oil the quantity of drying compound, which must be in fine powder, that it is thought best to employ. Manganese compounds, especially the borate, tend much more to gelatinise the oil on being heated too highly, than with lead compounds. As to the use of lead products, either litharge or red lead may be used, the former preferably. Two per cent. of the weight of oil is sufficient for ordinary purposes. In case the use of manganese is desirable, borate of manganese should be employed, but should not exceed ½ per cent. of weight of oil even ¼ per cent. may be sufficient to keep it transparent. Lead rosinate, manganese rosinate, lime rosinate, in fine powder act similarly, but must not be used in excess. Wood oil is seldom used by itself, but mostly in admixture with linseed oil to which it is claimed imparts a greater degree of elasticity, hardness, and imperviousness.

In a recent article on the manufacture of flat wall paints W. G. Scott makes some very useful suggestions regarding wood oil. He states that the regulation jellying-point is supposed to be 540° F., but the rate of heating has very much to do with it, for instance, long-continued heating at 392° F. (200° C.) to 450° F. (232·2° C.) converts it into an insoluble jelly; on the other hand, it may be heated quickly to 620° F. before it commences to string or thicken, and in some cases it will not jelly until cooled back to 540°. Only a few moments are required for the oil to thus solidify, after it begins to string, but if a certain amount of rosin, 2 or more lb. per gallon, be added just on the point of stringing, the reaction is prevented and the mixture remains liquid. Some driers accelerate and some retard the jellying of wood oil, and it is a knowledge of this action and the proper heat treatment which enables the varnish-maker and paint manufacturer to produce a wood oil, which will dry flat without a crystalline surface. A mixture of 80 per cent. treated wood oil and 20 per cent. of treated linseed oil forms an excellent vehicle for flat wall finishes. Pigments ground in this mixture are apparently too thick for the brush, but work as freely as oil and level out perfectly. Furthermore, the paint flats down to a surface free from brush marks and other imperfections.

Wax is an ingredient used in some of the flat wall finishes, and it adds greatly to the waterproofing quality. It is essential that a white wax be used, and good results are obtained with Japan wax. Paraffin wax may be used if desired, but it retards the drying.

A flat, waterproof wax-oil formula is as follows :—

32 gallons (251 lb). China wood oil. Heat to 420° F., then add 8 lb. Japan wax. Stir well, allow to cool to 320° F., then thin with 16 gallons wood turpentine. Finally add 1 gallon concentrated varnish drier.

This oil when ground with pigments dries with a dull egg-shell surface and the paint is exceedingly waterproof.

For a cheap " Factory White " the following pigments are ground in 1 gallon of the above oil :—

15 lb. lithopone.
4 lb. zinc oxide.
1 lb. asbestine pulp.

The paste so produced may then be thinned to brush consistency with more of the above wax oil, or reduced with turpentine or benzine. If preferred, whiting may be used in place of asbestine pulp, but the asbestine helps to hold the pigments in suspension. The wax also helps to hold up the pigment.

To make a China wood oil varnish for blending with the cheaper grades of linseed oil and rosin or soft copal and dammar varnishes, the following method appears to be best :—

Run through a mill and grind well together, 32 lb. varnish-makers' lime flour, 6 lb. hydrated oxide of manganese, 12 lb. powdered litharge, and 6 gallons boiled linseed oil. Set aside until required. In a varnish pot of 100 gallons capacity place 200 lb. crude China wood oil and heat slowly to between 160° and 180° C. Before the maximum temperature has been reached take pot from fire and stir in at once 15 lb. of the drying compounds above mentioned ; keep stirring until the driers are well incorporated, then return to fire and add 200 lb. rosin that has been melted in another kettle, but keep temperature well down to 160° C. When oil and rosin are well mixed, take pot from fire and thin in the usual way with turpentine or benzine to proper consistence, filter and store.

China Wood Oil Varnishes with Direct Method : Pale Furniture Varnish.—4 gallons varnish-makers' bodied linseed oil and 50 lb. pale rosin are heated in the kettle to a temperature of 140° to 150° C. (288° and 302° F.), the rosin being added after oil has reached 212° F. When the temperature of 150° C. (302° F.) has been reached, 6 lb. of the finely ground lime and driers in oil, above referred to, are stirred in, and when this has been taken up, 5 lb. of China wood oil is added and the boiling continued about 10 minutes, when pot is removed from fire and contents thinned in the usual way with turpentine or benzine or a mixture of these solvents, about 10 to 12 gallons being required. This batch will produce from 20 to 22 gallons, but at no stage of the process must the temperature exceed the maximum of 302° F. A harder drying but much darker varnish can be made by boiling raw oil and rosin together at a temperature of 280° C. (536° F.) to a thick consistency, then allowing the temperature to go down to 180° C. (356° F.), and stirring in the 6 lb. of drier in oil and the 5 lb. of China wood oil, in the same manner as is followed in the pale varnish.

Durable Air Drying Varnish for Outside Work.—50 lb. boiled linseed oil, 10 lb. China wood oil, and 40 lb. pale rosin are heated to 160° C. (320° F.). When the oil and rosin are well united, a mixture of 8 oz. litharge, 2 oz. hydrated oxide of manganese, and 4 oz. lime ground fine in 1 quart of boiled linseed oil, is stirred in, and the temperature kept between 300° and 320° F. until the driers are taken up, then the pot is taken from fire and the contents thinned with from 8 to 10 gallons turps, or a mixture of turps and benzine. This batch will produce from 20 to 22 gallons of a pale and fairly durable cheap outside varnish. The boiled linseed oil referred to is understood to be linseed oil boiled with drier, to the consistency of syrup of honey.

Japan Varnish with China Wood Oil.—To the initiated it is no secret, that ordinary rosin varnishes, no matter how much oil they may contain in proportion to the gum, are not well adapted for japanning on metals. This defect can be remedied to a great extent by the introduction of a small portion of wood oil. A varnish made by the following formula will dry in ordinary air in from 36 to 48 hours, but when placed in an oven will bake hard in 6 hours at a temperature of 180° F. without perceptible discoloration: 7 gallons bodied linseed oil and 8 lb. China wood oil are heated to 150° C. (302° F.), and while 4 lb. of the driers ground in oil are stirred in, the temperature is allowed to rise to 180° C. (356° F.) and held there until the driers are taken up, when 40 lb. hardened rosin, melted in another pot, are introduced, and when this is incorporated the pot is taken from fire and contents thinned down with 10 or 12 gallons turpentine. This batch will produce not less than 22 gallons of varnish.

How to Prepare China Wood Oil for Use as an Aid to Linseed Oil as a Paint Vehicle (not for Varnish Making).—The oil is placed in a portable varnish pot and heated over a moderate fire to a temperature of not over 180° C. (356° F.). As soon as it reaches that point, the pot is removed from the fire, and the driers well stirred into the oil. To do this effectually, without the pot on the fire, to risk loss of oil by gelatinising, the driers should be ground in enough linseed oil to form a thin semi-paste, so that the full benefit may be derived from the manner of introduction. For every 100 lb. of wood oil placed in the kettle, 1 lb. of litharge will be sufficient to make the oil become transparent and remain so on drying. If desired to give the boiled China wood oil extra drying properties, the quantity of litharge may be increased to 2 lb. for every 100 lb. of the oil. Or the litharge may the paint flats down to a surface free from brush marks and other imperfections.

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Hardening Rosin by Lime in the Actual Process of Varnish-making.—The hardening of rosin varnish by lime, in the actual process of varnish-making, may result in the thickening of the varnish, unless the operation is performed with the requisite precaution. Thus, if the temperature be insufficient, only part of the lime will dissolve, the insoluble portion forming thick lumps, which settle down when the varnish is thinned with the diluent. On the other hand, too little lime will leave the rosin insufficiently hardened, and therefore it will remain tacky when dry, whilst an excess of lime causes the mass to thicken considerably, and require timely treatment with linseed oil, wood oil, or rosin to restore its fluidity. The following recipe will be found to give satisfactory results: 10 parts of American rosin, $\frac{3}{4}$ part of marble lime in powder, 5 parts of boiled linseed oil, or wood oil, 5 parts of oil of turpentine and 5 parts of turpentine substitute. The rosin is heated to 270° C. (518° F.) in an enamelled cast-iron pan, and the lime is added in two portions, heating being continued until a thick, strong crust forms on the surface of the rosin. The oil is stirred in and the whole is heated till it froths up and a skin forms again. The pan being taken from the fire and left to cool, the contents are diluted, first with the oil of turpentine and then with the substitute. If a more consistent "varnish" is required, 0·35 part of litharge may be added at the outset, when the temperature has reached 230° C. (446° F.). If added after the lime, the litharge would greatly thicken the mass. The author of this process states that wood oil is preferable to linseed oil in making these varnishes, but a mixture of the two would no doubt give a far superior product.

[THE END]

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